VOL. VIII. [MARCH, 1886.] NO. 1.

AMERICAN

CHEMICAL JOURNAL.

THE ACTION OF HEAT ON LIQUID PARAFFINS.

BY L. M. NORTON AND C. W. ANDREWS.

The action of heat on the hydrocarbons of the aromatic series has often been studied, but such investigations in the fat series have been confined, with a single exception, to the gaseous hydrocarbons and mixtures of liquid paraffins of unknown composition. Thus, from the work of Thorpe and Young[1] on solid paraffin, of Wagner[2] on refined petroleum, of Liebermann and Burg[3] on petroleum vapors, of Letny[4] on petroleum residuum, of Prunier[5] on gasoline, and of Armstrong[6] and Williams[7] on the products of the Pintsch process for illuminating gas, no information can be gained in regard to the products of the decomposition by heat of any single hydrocarbon. Important investigations of the action of heat on methane, ethane, ethylene and acetylene have been made by Berthelot,[8] and on ethylene by Marchand[9] and Magnus.[10] Berthelot[11] included in his investigations pentane and amylene, and states that when heated in closed retorts to the temperature of the softening of the glass, they gave the lower hydrocarbons of the C_nH_{2n} and C_nH_{2n+2} series, and hydrogen.

[1] Ann. d. Chem. **165**, 1.
[2] Dingler, **217**, 64.
[3] Berichte d. deut. chem. Gesell. **11**, 723.
[4] Berichte d. deut. chem. Gesell. **11**, 1210.
[5] Ann. de Chim. et Phys. **5**, 17, 5.
[6] Journ. Soc. Chem. Ind. 1884, 462.
[7] Chem. News, **49**, 197.
[8] Berthelot, La Synthese Chimique.
[9] J. prak. Chem. **26**, 478.
[10] Pogg. Ann. **90**, 1.
[11] Ann. de Chim. et Phys. **4**, 9, 442.

It seemed to us that the action of heat on the liquid paraffins deserved further investigation, and we chose the normal hexane as presenting the most interesting and important study, and have extended our work to isohexane and normal pentane.

The hydrocarbons were prepared from petroleum by fractionation upon an industrical scale.[1] After careful fractionation in the laboratory with the aid of a Hempel's tower 70 cm. high, they were treated with bromine to remove double-bonded hydrocarbons, with fuming nitric acid to remove aromatic hydrocarbons, whenever these were present, dried, and subjected to a final fractionation.

The method of decomposition and purification of the products was essentially the same in each case. The hydrocarbon was decomposed by passing the vapor through a heated glass tube, 15 mm. in diameter, except in the case of isohexane, when a porcelain tube was used. The tube was heated in a combustion furnace 70 cm. long. The hydrocarbon was delivered in a slow stream from a drop-funnel. A pressure of carbonic acid was maintained upon the hydrocarbon to overcome a very annoying back pressure from the decomposition tube. The hydrocarbon was vaporised by the gentle heat in the part of the tube outside the furnace, and the vapors passed on through the tube. The products of the decomposition passed first through a tube one metre long surrounded by ice-water into a receiver also cooled by ice-water, and then through a shorter tube surrounded by a freezing mixture and delivering into the same receiver. By means of these two condensers nearly all of the products boiling above 10° were collected in the receiver. The uncondensed gaseous products from the second condenser were passed into an ammoniacal cuprous chloride solution to absorb all triple-bonded hydrocarbons, then through a dilute solution of acetic acid to retain any ammonia, and finally through a series of flasks containing a solution of bromine in bisulphide of carbon to absorb all double-bonded hydrocarbons. As in no case was any considerable precipitate found in the ammoniacal cuprous chloride solution, the products to be investigated were the liquid in the receiver and the bromides from the absorption flasks.

The former was first carefully fractionated, the portions were

[1] We desire to acknowledge our indebtedness to the Jenney Manufacturing Co. of South Boston, refiners, for their kind assistance.

then treated separately with bromine, and distilled. The bromides were then distilled under a very low pressure, but the quantities obtained were in all cases so small that no satisfactory purification could be made. The results of the analyses indicate, however, without much doubt, the presence of certain hydrocarbons.

The bromides from the absorption flasks were freed from any excess of bromine, and from the bisulphide of carbon, and then distilled under a very low pressure. The liquid bromides were thus separated from a tarry mass containing a solid bromide which could not be distilled, even under reduced pressure, without decomposition. The distillation was carried to the point at which decomposition began. The liquid bromides were then fractionated, and separate portions were analysed. The solid bromide was extracted from the tar by hot alcohol, crystallised from hot alcohol and sublimed until it showed a constant melting-point.

Normal Hexane.

The normal hexane boiled at 68° and had a specific gravity of 0.6745 at 18° compared with water at 4°. The decomposition was effected at a bright red heat, and was carried on very slowly, in order that it might be as complete as possible. Usually about 25 cc. were decomposed in an hour. Only traces of a precipitate were formed in the ammoniacal cuprous chloride solution, and after a short time the gases were allowed to pass directly from the condenser into the bromine solution.

The weight of the liquid in the receiver was one-tenth of the weight of hexane used. It contained about 12 per cent. of unaltered hexane and small quantities of double-bonded hydrocarbons boiling below 80°. Analysis of the bromides gave 68.17 per cent. bromine, and indicated a mixture of hexylene and amylene bromides. The small fraction boiling above 75°, after treatment with bromine, was proved, by the aniline test, to contain considerable benzol. Nitrobenzol was readily formed at 0°, hence it could not have been derived from hexhydrobenzol.[1] It is certain, therefore, that benzol can be obtained from hexane, though the yield is small. As no acetylene was found among the products of decomposition, it is most probable that the benzol was not formed by the action of heat upon acetylene. Besides hexane, benzol and double-bonded

[1] Weden, Ann. d. Chem. 187, 163.

hydrocarbons, the liquid contained very small quantities of saturated hydrocarbons boiling between 100° and 160°, and some tar.

The bromides from the absorption flasks could not be separated completely by long fractionation under ordinary and reduced pressure. The following analyses were made:

I. 0.1573 gram of portion boiling at 128°–130.5° gave 0.3138 gram of AgBr.

II. 0.3261 gram of portion boiling at 136° gave 0.6314 gram of AgBr.

III. 0.1648 gram of portion boiling at 140°–144° gave 0.3067 gram of AgBr.

	Calculated for $C_2H_4Br_2$.	Found. I.	Found. II.	Found. III.	Calculated for $C_3H_6Br_2$.
Per cent. Br	85.11	84.90	82.39	79.22	79.22

They are, therefore, ethylene and propylene bromides in nearly equal quantities. We were unable to detect the presence of butylene bromide.

The solid bromide crystallised in beautiful colorless needles, insoluble in water, which melted at 112°. Its composition was that of a tetrabrombutane.

I. 0.2154 gram of substance gave 0.0372 gram of H_2O and 0.1028 gram of CO_2.

II. 0.1125 gram of substance gave 0.2255 gram of AgBr.

III. 0.1196 gram of substance gave 0.2403 gram of AgBr.

	Calculated for $C_4H_8Br_4$.	Found. I.	Found. II.	Found. III.
C	12.84	13.01	...	...
H	1.60	1.91	...	...
Br	85.56	...	85.33	85.49

This tetrabrombutane closely resembles in its properties that obtained by Caventou[1] from the products of the decomposition of ordinary amyl alcohol at a red heat, and by Henninger[2] from the butine obtained from erythrite. If identical with this, its constitution is $CH_2Br.CHBr.CHBr.CH_2Br$. Furthermore, it should be identical with that obtained by Prunier[3] from the products of the decomposition of gasoline at a red heat, although Prunier considers his bromide to be derived from the hydrocarbon $CH_3.CH_2.C:CH$, while our compound cannot be derived from a triple-bonded

[1] Comptes Rendus 56, 646. [2] Bull. Soc. Chim. [2] 19, 145.
[3] Ann. d. Chim. et Phys. 8, 17, 12.

hydrocarbon. It seems probable, also, that it is identical with that obtained by Armstrong[1] from the condensed products of the Pintsch process and with that of Helbing[2] from the liquids of low boiling-point obtained in refining benzol.

The decomposition of hexane at a red heat gave, therefore, ethylene, propylene, butine, amylene, hexylene, benzol and gases not absorbed by bromine.

We next undertook to find the temperature at which this decomposition begins, and to investigate the products obtained at a comparatively low temperature. The apparatus used was the same as above described, except that the glass decomposition tube was surrounded by an iron pipe 5 cm. in diameter, and slightly longer than the combustion furnace. The temperature of the air in the pipe was determined approximately by means of a calibrated air-thermometer.[3] At 550° no gases were given off, and the hexane was recovered unchanged. At 600° the formation of gases was not observed, but the hexane recovered was found to contain traces of unsaturated compounds, indicating that decomposition had begun. At a little below 700° gases began to pass through the apparatus, and an investigation of the products at this temperature was made. They were collected as in the previous case. There was no precipitation in the ammoniacal cuprous chloride solution.

The liquid in the receiver began to boil at 57°, and was separated into portions boiling at 57°–64°, 64°–70° and 70°–80°. The bromide from the lowest portion contained 72.61 per cent. of bromine, and was probably a mixture of butylene and amylene bromides. Its specific gravity at 0° was 1.77, while that of butylene bromide is 1.8503, and that of amylene bromide 1.7087, at the same temperature.[4] The bromide from the portions boiling at 64°–80° contained 67.07 per cent. of bromine, and was probably a mixture of amylene and hexylene bromides.

The most careful tests failed to detect benzol in any of the fractions, and we are convinced that it is not formed from hexane at the temperature of the experiment. The chief constituent of the liquid was undecomposed hexane.

The bromides from the absorption flasks upon fractionation separated into two portions of tolerably constant boiling-points,

[1] Jour. Soc. Chem. Ind. 1884, 462. [2] Ann. d. Chem. 172, 291.
[3] Berthelot, Méchanique Chimique I, 301. [4] Saytzeff, Ann. d. Chem. 179, 332 and 308.

one at 140°–145°, the other, much smaller in quantity, at 150°–155°. The analysis resulted as follows:

I. 0.2448 gram of substance boiling at 140°–145° gave 0.4562 gram of AgBr.

II. 0.2370 gram of substance boiling at 150°–155° gave 0.4323 gram of AgBr.

	Calculated for $C_3H_6Br_2$.	Found. I.	Found. II.	Calculated for $C_4H_8Br_2$.
Per cent. Br	79.22	79.33	77.62	74.06

The second portion undoubtedly contained butylene bromide, but the quantity was not sufficient to permit its complete separation from the propylene bromide. Ethylene bromide was not observed. The solid bromide melted constantly at 116°, and proved upon analysis to be a tetrabrombutane.

I. 0.1073 gram of substance gave 0.2141 gram of AgBr.

	Calculated for $C_4H_8Br_4$.	Found.
Per cent. Br	85.56	84.92

The bromide was more easily purified than in the previous case, and we attribute the difference in melting-point to the greater purity of the latter product.

The decomposition of hexane at about 700° gave, therefore, propylene, butylene, amylene, hexylene, butine and gases not absorbed by bromine.

Isohexane.

The isohexane $CH_3.CH_2.CH_2.CH:(CH_3)_2$ was obtained by fractionation from gasoline. It boiled at 64°. A red heat was employed for its decomposition, and the only change in apparatus was the substitution of a porcelain tube 10 mm. in diameter for the glass one. A very slight deposit of carbon was formed in the tube. The products were collected as usual. The ammoniacal cuprous chloride solution showed traces of a precipitate.

The liquid in the receiver was fractionated into portions boiling at 40°–60°, 60°–76°, and a small residue above 76°. The bromide from the lowest portion boiled at 86°–90° under a pressure of 52 mm., and contained 73.2 per cent. of bromine. The bromide from the second portion boiled at 99°–102° under 42 mm. pressure, and contained 66.8 per cent. of bromine. The first was probably butylene bromide, and the second hexylene bromide with a little amylene bromide. The remainder of the liquid consisted of undecomposed isohexane and a small quantity of tar.

The bromides from the absorption flasks were separated from the solid bromide by distillation at the ordinary pressure. Portions boiling at 130.5°, 136° and 141.5° were analysed.

I. 0.3100 gram of portion boiling at 130.5° gave 0.6177 gram of AgBr.

II. 0.3333 gram of portion boiling at 141.5° gave 0.6231 gram of AgBr.

	Calculated for $C_3H_6Br_2$.	Found. I.	Found. II.	Calculated for $C_3H_4Br_2$.
Per cent. Br	85.11	84.8	79.5	79.22

The portion boiling at 136° contained 80.5 per cent. of bromine, indicating a mixture in which propylene bromide predominated.

The solid bromide was crystallised repeatedly from alcohol until it melted constantly at 107.5°. It crystallised in pearly scales.

0.2151 gram of substance gave 0.4322 gram of AgBr.

	Found.	Calculated for $C_4H_8Br_4$.
Per cent. Br	85.50	85.56

The low melting-point, which was not raised by sublimation, and the different crystalline form make it improbable that this bromide is identical with the one obtained from normal hexane.

The decomposition of isohexane at a red heat gave, therefore, ethylene, propylene, butylene, amylene, hexylene, butine and gases not absorbed by bromine.

Normal Pentane.

The pentane was obtained from petroleum by fractional distillation. It boiled between 35° and 37.5°; its specific gravity at 17° was 0.6323 compared with water at the same temperature. The apparatus and method of decomposition were the same as for normal hexane. The decomposition was more rapid and complete than in the case of hexane. Carbon was deposited in the decomposition tube. The ammoniacal cuprous chloride solution showed mere traces of a precipitate.

The amount of the liquid in the receiver was very small, about 6 per cent. of the pentane used, and the larger part of it was undecomposed pentane and tar. Unsaturated hydrocarbons were present, but in quantities too small for identification. Benzol was not present.

Portions of the bromides from the absorption flasks boiling at 128°–130° and 140°–144° were analysed.

I. 0.2040 gram of portion boiling at 128°–130° gave 0.4080 gram of AgBr.

II. 0.2281 gram of portion boiling at 140°–144° gave 0.4275 gram of AgBr.

	Calculated for $C_3H_6Br_2$.	Found. I.	Found. II.	Calculated for $C_3H_6Br_2$.
Per cent. Br	85.11	85.13	79.75	79.22

The solid bromide melted constantly at 113°, and was a tetrabrombutane.

I. 0.1079 gram of substance gave 0.2172 gram of AgBr.

II. 0.4118 gram of substance gave 0.1933 gram of CO_2 and 0.0620 gram of H_2O.

	Calculated for $C_4H_8Br_4$.	Found. I.	Found. II.
Br	85.56	85.67	...
C	12.84	...	12.80
H	1.60	...	1.68

We know no reason to doubt the identity of this tetrabrombutane with the one obtained from normal hexane.

The decomposition of normal pentane at a red heat gave, therefore, ethylene, propylene, butine, traces of other unsaturated hydrocarbons, and gases not absorbed by bromine. Berthelot[1] obtained, by the prolonged action of heat on pentane, methane, ethane and hydrocarbons C_nH_{2n+2} from propane to pentane, ethylene and hydrocarbons C_nH_{2n} from propylene to amylene, hydrogen, small amounts of tarry hydrocarbons and traces of acetylene. It is probable that the difference between these results is due to the different conditions of the experiments.

The comparative yield of the various products in these decompositions is shown by the following table:

	Normal Hexane, red heat.	Normal Hexane, 700°.	Isohexane, red heat.	Normal Pentane, red heat.
Hexylene,	very small	very small	very small	
Amylene,	very small	very small	traces	traces?
Butylene,	none	small	moderate	
Propylene,	large	large	large	large
Ethylene,	large	none	large	large
Butine,	small	small	small	small
Benzol,	small	none	none	none
Gases not absorbed by bromine,	large	moderate	large	large

[1] Ann. d. Chim. et Phys. 4, 9, 442.

The liquid paraffins furnish principally, under the conditions described, hydrocarbons of lower molecular weight. The relative amounts, however, vary with the temperature employed. The tendency to form by condensation hydrocarbons of higher molecular weight is very slight. The frequent occurrence of butines among the products of such decompositions makes a further study of their structure desirable.

In this investigation we have been ably assisted by Messrs. H. P. Talbot and H. W. Tyler, and we desire to acknowledge our great indebtedness to them.

Mass. Institute of Technology, Boston.

A NEW APPARATUS FOR MEASURING GASES AND MAKING GAS ANALYSES.

By E. H. Keiser.

In recent years the methods of gas analysis for industrial and technical purposes have been greatly simplified and improved, and are being used more and more extensively in manufacturing establishments. Much less progress has, however, been made in the more accurate scientific methods of gas analysis. While the labors of Orsat, Bunte, Winkler and Hempel have resulted in bringing the methods of industrial gas analysis to such a condition of perfection that the composition of any gas mixture may be determined with great rapidity, and with a degree of accuracy sufficient for all manufacturing purposes, nevertheless, when more accurate results are required, recourse must be had to the older eudiometric methods of Bunsen. Admirable as these methods are, it cannot be denied that great skill is required to carry them out, and to obtain good results, scrupulous attention must be given to all the minute details and precautions. The measurements being made in graduated eudiometers, it is necessary that the eudiometers should be calibrated, and tables of corrected readings constructed, before an analysis is made. There are inconveniences connected with the introduction and removal of absorbing reagents, and as solid reagents are nearly always used, the absorption

requires considerable time. In brief, the method is not at all adapted to making a series of rapid and yet accurate analyses.

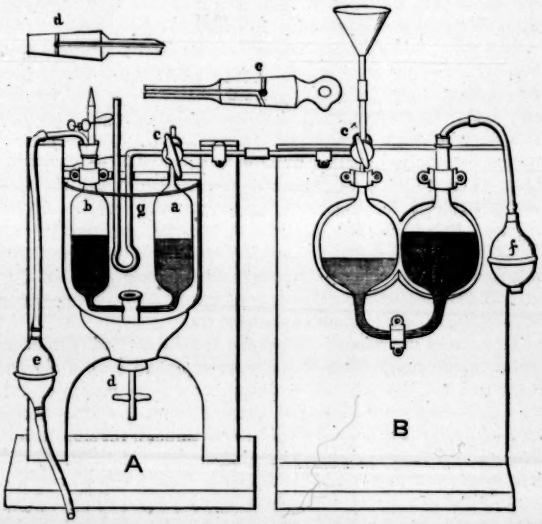
Numerous forms of apparatus have been devised to overcome the difficulties of the Bunsen method. Among others, Regnault and Reiset,[1] Frankland and Ward,[2] Doyère,[3] and recently Hempel,[4] have constructed instruments by means of which analyses can be made with as great accuracy as by the Bunsen method, and with much greater rapidity. Liquid instead of solid absorbing reagents are used, and the graduated measuring tubes are surrounded by water, so that an equality of temperature between the gas and water is rapidly obtained. All of these gas-measuring instruments are more or less complicated in construction. Graduated glass measuring tubes are used, thus necessitating a previous calibration. Most of them occupy a large space, and must be kept in separate rooms especially devoted to gas analysis.

It seemed therefore desirable to construct a simple gas-measuring apparatus which would be compact in form, which might be easily carried about and used at any place, and yet be capable of measuring gas volumes with great accuracy. Long graduated glass tubes and graduated vessels of all kinds were discarded, and an instrument was constructed upon the principle of determining the volume of a gas from the weight of mercury which it displaces at a known temperature and pressure. From the weight of mercury displaced the volume of the gas can be determined with much greater accuracy than by a direct reading on a graduated glass eudiometer.

The accompanying cut shows the construction of the measuring apparatus and the absorption pipette. *A* is the measuring apparatus, *B* is the absorption pipette; *a* and *b* are glass bulbs of about 150 cc. capacity. They are connected at the bottom by a glass tube of 1 mm. bore, carrying the three-way stop-cock *d*. The construction of the key of the stop-cock is shown in the margin. One hole is drilled straight through the key, and by means of this the vessels *a* and *b* may be made to communicate. Another opening is drilled at right angles to the first, which communicates with an opening extending through the handle, but does not communicate with the first opening. By means of this, mercury

[1] Regnault and Reiset, Ann. Chim. Phys. [3] **26**, 333.
[2] Frankland, Journ. Chem. Soc. 1868, 109.
[3] Doyère, Ann. Chim. Phys. [3] **28**, 1.
[4] Hempel, Analyse der Gase, Braunschweig, 1880.

contained in either *a* or *b* may be allowed to flow out through the handle *d* into a cup placed beneath. The bulb *b* is contracted at the top to an opening 20 mm. in diameter. This is closed by a rubber stopper carrying a bent glass tube, to which is attached the rubber pump *e*. To a second glass tube passing through the stopper, a short piece of rubber tubing with a pinch-cock is attached. By means of the pump *e* air may be forced into or withdrawn from *b*, as one or the other end of the pump is attached to the glass tube.



The bulb *a* terminates at the top in a narrow glass tube, to which is fused the three-way stop-cock *c*. The construction of the key of this stop-cock is also shown in the cut. By means of it the vessel *a* may be allowed to communicate with the outside air, or with the tube passing to the absorption pipette, or with the gauge *g*. The gauge *g* is a glass tube having a bore 1 mm. in diameter and bent, as shown in the figure. By pouring a few drops of water into the open end of this tube a column of water several centimeters high

in both limbs of the tube is obtained. This serves as a manometer, and enables the operator to know when the pressure of the gas equals the atmospheric pressure. To secure a uniform temperature, the bulbs *a* and *b* are surrounded by water contained in a glass vessel. This vessel for holding water is merely an inverted bottle of clear glass from which the bottom has been removed. The handle of the stop-cock *d* passes through a rubber stopper in the neck of the bottle. A thermometer graduated to $\frac{1}{5}°$ is placed in the water near the bulb *a*. The whole apparatus is supported upon a vertical wooden stand.

The absorption pipette *B* consists of two nearly spherical glass bulbs of about 300 cc. capacity. They communicate at the bottom by means of a glass tube, 3 mm. inside diameter. *c'* is a two-way stop-cock. The holes in the key are drilled at right angles, so that the tube which connects with the measuring apparatus may be put in communication either with the funnel or with the absorption bulb. The funnel is of service in removing air from the tube which connects the measuring apparatus with the absorption pipette. By pouring mercury or water into the funnel and turning the stop-cocks *c'* and *c* in the proper directions all the air is readily removed. *f* is a rubber pump used in transferring gas from *B* to *A*. The lower part of the pipette contains mercury, which protects the reagent from the action of the air.

To measure the volume of a gas the vessel *a* is filled completely with pure mercury. This is easily accomplished by pouring the mercury into *b*, and then, after turning *c* until *a* communicates with the outside air, forcing it into *a* by means of the pump *e*. Any excess of mercury in *b* is then allowed to flow out through the stop-cock *d*. When *a* and *b* are now placed in communication the mercury will flow from *a* to *b*, and gas will be drawn in through the stop-cock *c*. The volume of mercury which flows into *b* is equal to the volume of gas drawn into *a*. When the mercury no longer rises in *b*, and it is desired to draw in still more gas into *a*, then it is only necessary to exhaust the air in *b* by means of the pump *e*. After the desired quantity of gas has been drawn into *a* the stop-cock *c* is closed. After standing a few minutes the temperature of the gas becomes the same as that of the water surrounding *a*. The pressure of the gas is then made approximately equal to atmospheric pressure by allowing the mercury to flow out of *b* into a weighed beaker placed beneath the stop-cock *d* until it stands at nearly the same level in

both *a* and *b*. Communication is now established between *a* and *g*, and by means of the pump *e* the pressure can be adjusted with the utmost delicacy until it is exactly equal to atmospheric pressure. The stop-cock *d* is then closed, and the remainder of the mercury in *b* is allowed to flow out into the beaker. The weight of the mercury displaced by the gas divided by the specific gravity of mercury at the observed temperature gives the volume of the gas in cubic centimeters.

If it is desired to remove any constituent of the gas by absorption, a pipette *B*, containing the appropriate reagent, is attached to the measuring apparatus. All the air in the connecting tube is expelled by pouring mercury into the funnel and turning the stop-cocks *c'* and *c* so that the mercury flows out through *c*. A little more than enough mercury to expel the gas in the vessel *a* is poured into *b*. The small quantity of air which is confined in the tube connecting *b* with the stop-cock is removed by allowing a few drops of mercury to run out through *b*. Then *a* and *b* are placed in communication. The stop-cocks *c* and *c'* are turned so that the gas may pass into the pipette, the mercury which filled the connecting tube passes into the absorbing reagent and unites with that which is already at the bottom of the pipette. The transfer is facilitated by the pump *e*. After absorption the residual volume is measured in the same way that the original volume was measured. *a* is completely filled with mercury from the upper to the lower stop-cock, and all the mercury in *b* is allowed to run out; the gas is then drawn back into the measuring apparatus, the last portion remaining in the connecting tube being displaced by means of mercury from the funnel. The volume is then determined as before.

The calculation of the results of an analysis is very simple. If the temperature and pressure remain the same during an analysis, as is frequently the case, then the weights of mercury obtained are in direct proportion to the gas volumes, and the percentage composition is at once obtained by a simple proportion.

If the temperature and pressure are different when the measurements are made, it is necessary to reduce the volumes to 0° and 760 mm. The following formula is then used:

$$V' = \frac{W(H-h)}{D(1+.00367\times t)760},$$

in which

W = weight of mercury obtained (in grams),
D = specific gravity of mercury at $t°$,
t = temperature at which the gas is measured,
H = height of the barometer,
h = tension of aqueous vapor,
V' = reduced gas volume (in cubic centimeters).

In all the measurements made with the apparatus the gas is saturated with aqueous vapor, because it comes in contact with the water in the manometer g.

The following experiments were made to test the accuracy of the instrument. A quantity of air was drawn into the measuring bulb and its volume determined. The air was then transferred to an absorption pipette which contained only mercury and no reagent. It was then brought back again into the measuring apparatus and its volume redetermined. The following results were obtained:

I.

	Volume at 0° — 760 mm.
Volume of air taken,	57.558 cc.
" after first transfer,	57.567
" " second transfer,	57.570

II.

	At 0° — 760 mm.
Volume taken,	93.216 cc.
" after transferring,	93.229

III.

	At 0° — 760 mm.
Volume taken,	133.473 cc.
" after transferring,	133.490

IV.

	At 0° — 760 mm.
Volume taken,	92.275 cc.
" after transferring,	92.260

V.

	At 0° — 760 mm.
Volume taken,	109.025 cc.
" after transferring,	109.020

VI.

	At 0° — 760 mm.
Volume taken, ...	103.970 cc.
" after first transfer, ...	103.955
" " second transfer, ...	103.980

The apparatus was also tested by making analyses of atmospheric air. It has been shown that the composition of the air varies from day to day.[1] This variation is sometimes as much as .5 per cent. The causes which produce these fluctuations in the composition of the atmosphere are at present but imperfectly understood. It is therefore desirable to have some simple instrument by means of which the composition of the air may be determined rapidly and yet with great accuracy.

The following analyses show that the apparatus here described is well adapted to this purpose. The reagent used to absorb the oxygen and carbon dioxide was an alkaline solution of pyrogallol, prepared by mixing one volume of a 25 per cent. solution of pyrogallol with six volumes of a 60 per cent. solution of potassium hydroxide.

Analysis of Air taken from the Laboratory.

I.

	W	H	t	V′	Per cent. $O + CO_2$.
Air taken,	1738.53	743.37	15.8	116.435 cc.	...
Vol. of nitrogen,	1377.62	743.37	15.8	92.264	20.760
" "	1376 40	743.55	15.75	92.255	20.771

Per cent. of oxygen and carbon dioxide, 20.765.

II.

	W	H	t	V′	Per cent. $O + CO_2$.
Vol. of air,	1708.01	748.08	15.0	115.546 cc.	...
" nitrogen,	1356.04	747.33	15.2	91.564	20.755

Per cent. of oxygen and carbon dioxide found, 20.755.

The following analyses were made with a sample of atmospheric air collected on a subsequent day :

I.

	W	H	t	V′	Per cent. $O + CO_2$.
Vol. of air,	1704.81	754.92	12.2	117.814 cc.	...
" nitrogen,	1348.33	754.78	12.08	93.216	20.877
" "	1344.71	755.92	11.7	93.229	20.868

Per cent. of oxygen and carbon dioxide, 20.872.

[1] Winkler, Industrie Gase 2, 405. Hempel, Berichte der deutsch. chem. Gesell. **18**, 267.

II.

	W	H	t	V′	Per cent. O + CO_2.
Vol. of air,	1669.39	756.30	10.15	116.584 cc.	...
" nitrogen,	1323.24	755.49	10.05	92.260	20.863
" "	1322.38	755.30	10.00	92.252	20.870

Per cent. of oxygen and carbon dioxide, 20.866.

The apparatus described in the preceding pages was made for the author, in most excellent manner, by Mr. Emil Greiner, 79 Nassau street, New York.

BRYN MAWR, PA., *December*, 1885.

THE TITRATION OF ACID TUNGSTATES.

BY HERMAN SCHMIDT.

In No. 13 of the "Berichte der deutschen chemischen Gesellschaft," G. v. Knorre publishes some observations on the titration of acid tungstates, or as he calls them, paratungstates. As I have been engaged in the same line of research, I feel prompted to publish the results thus far obtained, in order to indicate my right to labor in this field.

When the salt $12WO_3 5Na_2O + 28Aq$ is dissolved in boiling water, the resulting solution has an acid character towards certain indicators. When phenolphthalein and rosolic acid are used, the solution reveals its acid nature; with cochineal solution and orange No. 3, however, the solution is alkaline. The investigation was undertaken in the hope that an acid tungstate might serve as an agent for standardising an alkaline solution. The preliminary results justified this belief, but an extended investigation revealed its fallacy.

2.0840 grams of the pure salt, in which the ratio is 12 of WO_3 to 5 of Na_2O, were dissolved and the solution was diluted to 500 cc., and portions of 50 cc. each were used for experiment. With an ammonia solution and phenolphthalein the change of color is very indistinct. A caustic soda solution containing .6471 gram Na_2O to 100 cc., and a chlorhydric acid solution containing .3478 gram HCl to 100 cc. were used.

Using phenolphthalein as the indicator, 50 cc., containing .2084 gram salt, required 1.25 cc. of the NaOH solution to give a distinct change. The purplish pink color remained unchanged for a minute or two, and then vanished. Successive additions of .02 cc. of alkali restored the color, which vanished again after each addition. This showed conclusively that the titration must be conducted in some other manner.

To determine, however, whether the first change of color was constant for successive titrations, and whether a saturating power corresponding to a definite salt—viz. $12WO_3(5+x)Na_2O$, in which x is an integer between 1 and 7, was indicated, the following experiments with this same solution were made:

Volume of the Solution.	$12WO_3\,5Na_2O+28Aq$ contained.	Soda Solution required.
50 cc.	.2084 gram.	1.25 cc.
"	"	1.26
"	"	1.25

Mean = 1.253 cc. soda solution = 3.88 per cent. Na_2O.

Since the crystallised salt contained 13.62 per cent. H_2O, to calculate the per cent. of Na_2O for the anhydrous salt, the per cent. found must be multiplied by the factor $\frac{100.00}{86.38}$. Result, 4.49 per cent. Na_2O. The ratio which approaches most nearly to this result is $2Na_2O$ for each molecule of $12WO_3\,5Na_2O$, which ratio expressed in percentage is 4.01 per cent. These experiments were performed with cold solutions. When the solution to be titrated was boiled and alkali added until the color appeared, no closely concordant results could be obtained.

If an excess of alkali was added and the solution then boiled, and the excess of alkali neutralised with chlorhydric acid, and alkali again added until the color was just restored, concordant results were obtained. In each case the amount of alkali required to color the same volume of pure water with the same amount of indicator is subtracted from the burette reading.

Experiment.

Volume of the Solution.	Salt contained.	Soda Solution required.
50 cc.	.45863 gram.	8.58 cc.
"	"	8.62
"	"	8.62

Mean = 8.61 cc. = 14.06 per cent. Na_2O.

Calculated on the weight of anhydrous tungstate employed.

Titration with the Use of Aurine as the Indicator.

Volume of the Solution.	Salt contained.	Soda Solution required.
50 cc.	.45863 gram.	8.56 cc.
"	"	8.62
"	"	8.60

Mean = 8.593 cc. = 14.03 per cent. Na_2O.

The molecular weight of $12WO_3\,5Na_2O$ is 3094. If then $Na_2O.WO_3$ is a neutral salt, seven molecules of $Na_2O = 434$ are necessary to saturate this acid salt; hence it requires for saturation $\frac{434}{3094} = 14.03$ per cent. Found, 14.06 per cent. and 14.03 per cent. Na_2O.

Upon investigating the subject further it was found that the time during which the solution of the tungstate was boiled with the excess of alkali materially influenced the results of the titration. The following titrations were made with a soda solution containing .2904 gram Na_2O in 100 cc., and a sulphuric acid solution of which 100 cc. corresponded to .2829 gram Na_2O.

8.2832 grams of the crystallised salt $12WO_3\,5Na_2O + 28Aq = 7.1385$ grams of the anhydrous salt were dissolved and the solution diluted to 1000 cc. Portions of 50 cc. each were used for experiment.

Experiments.

No.	Volume of the Solution.	Salt contained.	Alkali required.
1	50 cc.	.41416 gram.	17.27 cc.
2	"	"	17.17
3	"	"	17.25
4	"	"	17.26
5	"	"	17.11
6	"	"	17.04
7	"	"	17.27
8	"	"	17.24
9	"	"	17.26

Mean = 17.21 cc. = .4998 gram $Na_2O = 14.00$ per cent.

Titrations Nos. 5 and 6 are somewhat low compared with the others. In each experiment the solution was boiled about fifteen minutes with the excess of alkali before neutralising with acid.

Experiments.

6.5325 grams of the crystallised salt = 5.6271 grams of the anhydrous salt were dissolved and the solution diluted to 1000 cc.

No.	Volume of the Solution.	Salt contained.	Alkali required.
1	50 cc.	.32663 gram.	13.52 cc.
2	"	"	13.55
3	"	"	13.49
4	"	"	13.16
5	"	"	13 50
6	"	"	13.53
7	"	"	13.13

Mean of the titrations = 13.41 cc. = .3894 gram Na_2O = 13.86 per cent.

If we reject Nos. 4 and 7, which are low, the mean is 13.52 cc. = .3928 gram Na_2O = 13.97 per cent.

This is hardly justifiable, since all titrations were made in the same way and boiled approximately for the same length of time—viz.: fifteen minutes.

In the following series the time of boiling was slightly varied, as will appear from the fifth column.

7.5467 grams of the crystallised salt = 6.5015 grams of the anhydrous salt were used.

All the titrations were performed as in the foregoing experiments, only in Nos. 1 to 8 inclusive a chlorhydric acid solution was used to neutralise the excess of alkali, and in titrations 9 to 18 oxalic acid was used.

Experiments.

No.	Volume of the Solution.	Salt contained.	Alkali required.	Time of boiling.
1	50 cc.	.37733 gram.	15.96 cc.	12 minutes.
2	"	"	15.97	15
3	"	"	15.68	15
4	"	"	15.88	15
5	"	"	15.90	15
6	"	"	15.86	15
7	"	"	15.86	15
8	"	"	15.99	15
9	"	"	15.70	15
10	"	"	15.87	15
11	"	"	15.81	17
12	"	"	15.91	15
13	"	"	15.93	15
14	"	"	15.95	17
15	"	"	16.04	15
16	"	"	15.88	15
17	"	"	15.90	15
18	"	"	15.92	15

Mean of titrations = 15.89 cc. = .4614 gram Na_2O = 14.19 per cent.

This percentage is .16 in excess of the theoretical amount. This is easily explained; for if the tungstate solution mixed with the excess of soda is boiled less than twelve minutes, the percentage indicated will be very much too low; if the solution is boiled longer than seventeen minutes the result will be too high.

Thus, after titration No. 1 of the foregoing series was completed, alkali was again added to the solution, and after boiling, the excess was neutralised. 16.30 cc. were then indicated = 14.56 per cent. Na_2O. Alkali was again added, and after boiling the excess was neutralised. 16.38 cc. were then indicated = 14.63 per cent. Na_2O. After titration No. 9 of the foregoing series was completed an excess of alkali was added, and the solution boiled thirty minutes; after neutralising, 17.10 cc. in all of the soda solution were required = 15.27 per cent. Na_2O, when theory required 14.03 per cent. The following titrations will also show that the tungstate may be supersaturated with alkali, and the excess not be indicated by the phenolphthalein solution.

a) To 50 cc. of a solution containing .23196 gram $12WO_3 5Na_2 + 28Aq$ an excess of soda was added, and the solution allowed to stand at the temperature of the room. After four days the excess of alkali was neutralised, and .03398 gram Na_2O = 14.65 per cent. had been saturated. To the same solution an excess of alkali was again added, and after three days the excess was again neutralised. The total amount of alkali indicated was 15.01 per cent.

b) To 50 cc. containing .23196 gram $12WO_3 5Na_2O + 28Aq$ an excess of soda was added. After three days .03595 gram Na_2O = 15.50 per cent. had been saturated. Adding alkali again, and neutralising after six days, .03923 gram Na_2O = 16.91 per cent. were consumed.

It would be interesting to see whether the salt $Na_2WO_4 2H_2O$ would result by evaporating and crystallising the solutions.

After 24 hours, at the ordinary temperature, the normal saturation is usually complete, when the alkali is added to the cold tungstate solution. Thus: 50 cc. containing .56271 gram $12WO_3 5Na_2O + 28Aq$ were mixed with an excess of alkali, and after 24 hours the excess was neutralised. .03944 gram = 14.02 per cent. Na_2O were required for saturation.

In another experiment .03969 gram = 14.11 per cent. Na_2O were required for saturation.

The evidence is complete that the salt above titrated in its anhydrous state has the formula $12WO_3.5Na_2O$, and is a member of the metatungstate series to which Dr. Gibbs[1] has added a new member, $16WO_3.3Na_2O.4(NH_4)_2O + 8Aq$, the highest yet discovered. It may still be interesting, however, to observe that all the above titrations agree better with the 12:5 than with the 7/3 ratio. If $7WO_3.3Na_2O$ were the formula of the anhydrous salt, then four molecules of Na_2O would be required for saturation. These four molecules, expressed in percentage of the anhydrous salt, are 13.70 per cent. Na_2O. The mean of all the titrations, 14.03, 14.06, 14.00, 13.86, 14.19 per cent. is 14.03 per cent., which is the percentage required by the 12:5 salt.

To a boiling solution of the normal tungstate $Na_2WO_4 + 2Aq$ ordinary acetic acid was added in excess. By the addition of alcohol an oil was precipitated, which readily changed into a crystalline mass. After two crystallisations the product was titrated.

Under these circumstances[2] one of two salts is produced. One has the constitution $10WO_3.4Na_2O + 23H_2O$, and the other agrees best with the formula $22WO_3.9Na_2O + 51Aq$. Just which was produced in the case I had not the means to decide, as I lacked facilities for quantitative work. The salt on ignition lost 13.79 per cent. H_2O. The salt $10WO_3.4Na_2O + 23H_2O$ requires 13.88 per cent. H_2O; and the formula $22WO_3.9Na_2O + 51Aq$ requires 13.95 per cent.

Of this salt 5.0009 grams were dissolved, and the solution was diluted to 1000 cc., and 50 cc. were used for each experiment. The titrations were performed exactly as in the foregoing series with the 12:5 salt. Oxalic acid was the standard acid solution employed.

Experiments.

	Time of Boiling with excess of Alkali.	Volume.	Salt present.	Alkali required.
1	15 minutes.	50 cc.	.25005 gram.	10.48 cc.
2	15	"	"	10.48
3	20	"	"	10.52
4	20	"	"	10.73
5	18	"	"	10.50
6	15	"	"	10.43
7	20	"	"	10.48
8	18	"	"	10.38
9	20	"	"	10.45
10	20	"	"	10.53
11	15	"	"	10.18

[1] Proceedings of the Am. Academy, 1885. [2] Gibbs, *Ibid.* 1879, pp. 5, 9.

Titration No. 4 is somewhat high, and No. 11 low. No regularity is discernible in the increase of alkali as the time of boiling is increased. As the titrations were made in the same way, equal weights attach to each of them, and it would not be justifiable to reject either No. 4 or 11.

Mean of the eleven titrations = 10.47 cc., corresponding to .06150 gram Na_2O = 14.26 per cent., which were required to saturate the anhydrous salt.

The formula $10WO_3 4Na_2O$ requires 6 molecules of Na_2O for saturation. This amount expressed in percentage = 14.49 per cent. Na_2O.

The anhydrous salt $22WO_3 9Na_2O$ requires 13 molecules Na_2O for saturation, or 14.24 per cent. Na_2O.

The percentage of sodic oxide found, 14.26 per cent., agrees best with 14.24 per cent., the amount required by the 22/9 ratio.

It may be observed that neither haematoxylin nor purpurin can be used in these titrations.

Attempts were made to use a solution containing a known weight of pure 12 : 5 tungstate of soda instead of the standard acid solution. No results whatever could be obtained by titrating either in hot or cold solutions. This might have been foreseen, for no closely concordant results could be obtained by saturating a hot acid tungstate solution with an alkali—*i. e.*, adding the alkali until the indicator showed the excess.

Qualitative experiments seem to show that boiling solutions of acid vanadates can be titrated, using either aurine or phenolphthalein as the indicator, and performing the titration as in the case of the acid tungstates.

An excellent end reaction, but no concordant results are obtained when an alkali is added to a cold solution of the 14 : 6 molybdate of ammonium, using aurine as the indicator. Phenolphthalein, on account of the ammonia liberated, would not apply. If the molybdate solution had been boiled with the excess of soda, so that all the ammonia had been driven off, and then the excess of alkali neutralised, perhaps satisfactory results would have been obtained.

I am greatly indebted to Dr. Wolcott Gibbs for the selection of the subject and the many kind suggestions in connection with this work.

CLEVELAND, IA., *Nov.* 26, 1885.

Contributions from the Chemical Laboratory of Harvard College.

XLVII.—A THERMOCHEMICAL ANALYSIS OF THE REACTION BETWEEN ALUM AND POTASSIUM HYDRATE.

By A. V. E. Young.

PART I.

In the course of a thermochemical study of potassic aluminate, I desired to use as one element of calculation the amount of heat evolved in the following reaction,

$$Al_2(SO_4)_3.K_2SO_4 + 6KOH = 4K_2SO_4 + Al_2(OH)_6,$$

assuming, in accordance with Thomsen's statement, that the alum is equivalent, for this purpose at least, to aluminic sulphate. This quantity is given by Thomsen[1] as 30.528 Calories. He determines it directly by precipitation with potassic hydrate in the calorimeter, and, as a control, determines the heat of precipitation with three molecules of baric hydrate. The results of the two methods agree fairly well. This value is made by the same author the basis for the indirect determination of the formation heat of the chloride and several other compounds of aluminum, and this notwithstanding the fact that he notes the complete precipitation of the aluminic oxide by five molecules of potassic hydrate instead of six, which would appear to indicate the formation of a basic precipitate. He evidently assumes that the addition of six molecules of the hydrate leaves the precipitate free of sulphuric acid, and that the agreement with the result obtained when baric hydrate is used affords confirmation of the assumption. Indeed, in other instances—*e. g.*, sulphates of copper, cobalt and cadmium—when the two methods do not give concordant results, he adopts the result by baric hydrate, and rejects that by potassic hydrate as being untrustworthy by reason of the formation of a basic precipitate. It would seem unsafe to assume, without experimental verification, that baric hydrate may not produce a basic precipitate as well as potassic hydrate, and thus render both methods open to the same objection.

However this may be, the results which I obtained soon led to the suspicion that the reaction with potassic hydrate was not so

[1] See Thermochemische Untersuchungen **1**, 366.

simple as is indicated by the above equation. One question after another arising which I was unable to answer, I have been led step by step to what may be called a thermochemical analysis of the reaction in question. The first part of the results obtained constitutes the substance of the following paper. At a later date I hope to publish a determination of the precipitation heat of aluminic hydrate by a method free from these objections. The first series of experiments involves the determination of the reaction heat of alum and potassic hydrate, the proportion of the latter present varying from .5 to 10 molecules. This is followed by a parallel series determining the composition of the precipitates obtained in the calorimetric experiments. Before considering in detail the results of the first series, I give a brief description of the calorimetric methods and of the calculations that were used.

Methods and Calculations.

The general method of heat measurement is that described by Berthelot. The calorimeter used was made after the specifications given by him,[1] without essential variation. The inner platinum calorimeter has a capacity of somewhat more than 1200 cc. The stirrer is a simple one, a piece of platinum foil fused to a glass rod. The thermometers were made by Baudin, of Paris, especially for thermochemical work, after specifications by Berthelot,[2] and were calibrated by Pernet at the Bureau International des Poids et Mesures. The zero points have been recently redetermined. The three pairs of duplicates taken together give a range of temperature from 0° to 33° C. They are graduated to fiftieths of a degree, and the readings were made, usually with the aid of a small hand lens, to $\frac{1}{100}$ of a degree, and often to $\frac{1}{200}$. The experiments were performed in a large basement room without artificial heat, where, during a portion of the year at least, the temperature conditions were fairly satisfactory. The operation consisted, with but one or two exceptions, in mixing in the calorimeter two portions of liquid of 500 cc. For this measurement two flasks were used, their graduation being verified by weight.

Solutions containing the requisite quantity of constituents were prepared, diluted to somewhat less than 500 cc., and allowed to stand in closed flasks beside the calorimeter until the following day, or perhaps during a longer interval. When ready for the

[1] Essai de Mécanique Chimique **1**, 140.

[2] *Ibid.* p. 164.

calorimetric determination, one of the prepared solutions was transferred with rinsing to the measuring-flask (care being taken not to change unduly its temperature in the handling) and filled to 500 cc. with distilled water that had stood a day or longer on the same table. It was then poured into the calorimeter and its temperature taken, after thorough stirring, at intervals of five minutes. The change of temperature during this interval should not be more than .02°. At the same time, the second solution having been transferred to the second measuring-flask, its temperature in the flask was taken by a second thermometer in similar manner. Its change likewise should not be more than .02° per interval of five minutes; and it is also important that it should be close to that of the room, which was read from an ordinary thermometer.

When the temperature conditions were satisfactory, and the readings duly recorded, the contents of the second flask were poured as quickly as possible into the calorimeter, the mixture thoroughly stirred, and the resultant temperature recorded. The interval between the last reading of the initial temperatures and the first of the resultant temperature was in this series of experiments one and a half or two minutes, and with few exceptions the maximum temperature was reached in this time. Readings were then taken, always with stirring, every minute for about five minutes, and then at an interval of five minutes, in order to have a record of the rate of cooling.

There seems to be one unsatisfactory point in this method of manipulation—namely, the difficulty of obtaining the true temperature of the second volume of liquid while it still remains in the flask, and of transferring it to the calorimeter without consequent change. Experience will convince one of this difficulty in experiments where a variation of .01° is of considerable importance. My habit is to close the flask and shake it as thoroughly as possible before inserting the thermometer, and to see that its temperature at the time shall be such that it need not be left more than five or ten minutes before transferring to the calorimeter. Meantime the flask stands in a loose bag of flannel, supported by a frame that serves as handle, so that the hand itself is distant several inches from the flask. Nevertheless, I have not infrequently obtained apparently accidental results which varied from the mean notably more than the average variation, and of which the difficulty just described seems the probable cause. I

hope later on to reduce, if not to eliminate, this uncertainty by a simple modification of apparatus.

Calculations.—The unit of heat employed, the Calorie, is the quantity required to raise one kilogram of water one degree at the temperature of the experiment. The mean temperature after mixing is calculated by the following formula:

$$T_m = \frac{(A+d)\,T_a + B(T_b - t)}{A+d+B};$$

in which

T_m = mean temperature.
A = water equivalent in grams of solution A in calorimeter.
d = water equivalent in grams of calorimeter, stirrer and thermometer.
B = water equivalent in grams of solution B.
T_a = observed initial temperature of solution A in calorimeter.
T_b = observed initial temperature of solution B in flask.
t = correction in degrees to make the reading of the two thermometers correspond.

The temperatures T_a and T_b, recorded in the tables, are those actually observed. In the calculation of T_m the correction d is used, but no correction is made for difference between the observed zero and the actual zero, as it would not affect the final result. The temperature recorded as T_c is the difference between the calculated mean temperature and the resultant temperature—in other words, the change of temperature due to the reaction—and is positive unless otherwise specified.

The column f in the tables gives the factor by which T_c is multiplied to reduce the heat disturbance of the reaction in Calories to molecular proportions, and H is this final result. The factor f is obtained as follows:

$$f = (A+B+d) \times \frac{\text{mol. wt.}}{\text{grms. taken}} \text{ (of alum).}$$

In all the experiments of this paper the water equivalent of the calorimeter and its belongings is 8.5 grams, while A and B are the volumes in cubic centimeters of the constituent solutions reckoned as grams of water (Berthelot's method of calculation[1]), each numerically equal to 500 cc., unless otherwise specified. $t = .008°$.

Limit of Error.—The reading of temperature is by far the most considerable element limiting the certainty of experimental observation. The quantity of alums used, 20.667 grams, is weighed

[1] Essai de Mécanique Chimique **1**, 190.

to one part in more than twenty thousand. The KOH solution is titrated against oxalic acid, and its titration confirmed gravimetrically. The quantity used in an experiment varied from 10.67 cc. to over 200 cc. This was measured in a burette to .05 cc., which would make the maximum variation considerably less than one per cent. of the quantity measured, even when the latter was at its minimum. Whereas, if we put the limit of temperature reading at .005°, and consider that the change in temperature depends upon three separate readings, the maximum of error should be .01°; or .005°, putting the limit of reading at .0025°. This would be a very large per-cent. variation in many of the experiments when the quantity measured falls considerably below 1°. Inspection of the tabulated data will show that in many cases the observed variation of T_e is much smaller than the calculated maximum—*e. g.*, the first six experiments of Table I, where it is only .001°. In most of the experiments a variation of .005° in T_e makes a variation of .24 Cal. in H.

Series I.

The numerical data of these experiments are recorded in Table I. The alum used was the commercial article, well crystallised and free of iron. Of it 20.067 grams were used in each experiment, and the solution prepared as already described. The proportion of water was about 2600 molecules to one of alum; in Thomsen's experiments, 2400. In column h is recorded the rate of heat disturbance per molecule of KOH. The results H and h are seen graphically expressed in Plate I, where x is the number of molecules of KOH added, and y in Line I represents H, in Line III, $h \times 10$.

Inspection of Line I shows that the heat evolution increases with the quantity of KOH, reaching a maximum at $x = 6$ or 6.5, and from this point diminishes until $x = 10$, when the resolution of the precipitate in the excess of KOH is complete. This means that the solution of the precipitate in excess of KOH is accompanied by heat absorption, or is endothermic. It will be shown farther on that the addition of KOH beyond $x = 8.5$ causes no further heat disturbance, and that 8.13 mol. KOH completely redissolve the precipitate; hence, in constructing the line, the value of y at $x = 8.13$ is made the same as at $x = 10$.

Line III reveals still more. It shows a constant rate of heat

evolution per molecule of KOH from $x=5$ to $x=1$. At this point it drops abruptly. Now, in the analytical part it will be shown (see Plate II, Line V) that precipitation begins between $x=1$ and $x=1.5$, probably at $x=1.13$. Hence, in constructing Line III the minimum is put hypothetically at $x=1.13$ instead of at $x=1.5$, which is the point actually determined. Inasmuch as the precipitate at first produced redissolves in excess of alum up to $x=1.13$, the drop in the line at this point indicates, probably, that this resolution also is accompanied by heat absorption. This will be evident upon considering that the heat disturbance, h, is a positive resultant, made up of both positive and negative elements. The principal positive element is the formation heat of potassic sulphate, and since this in all probability remains approximately constant for equal portions of KOH entering into combination, it follows that the negative element increases at the point $x=1.13$ in consequence of precipitation. In other words, precipitation is accompanied by heat evolution, and resolution of the precipitate by heat absorption.[1]

Beyond $x=1.13$ there is evidently a tendency to rise slightly up to $x=5$, or thereabouts. The break at $x=4.8$ is within the limit of error, since the larger value recorded in Table I gives the alternative point $x=4.8$ just above the line, as seen in the plate. Indeed, the increase between $x=1.13$ and $x=5$ depends upon differences which lie so close to the limit of experimental error that one must hesitate to consider it more than probable. It would be interesting to establish it beyond doubt, in view of the analytical results shown in Plate II, Line VII. There can be no doubt, however, that the line drops beyond $x=5.12$, as would be expected.

It is to be noted that the maximum in Line I occurs at $x=6$ or 6.5, while in Line III it occurs at $x=5$, which is the point at which the aluminic oxide is completely precipitated. This leads to the question, What causes the continued heat evolution after the precipitation is total? the discussion of which must be deferred until the analytical results have been described. The three experiments recorded in Table III serve, however, to fix one point bearing thereon. 4.8 mol. KOH were added to one of alum in the usual conditions. Then to this mixture were added in the calorimeter the remaining 1.2 mol. KOH, in the proportionate

[1] See similar case of lead, Thomsen **1**, 377.

quantity of water, and the heat evolution measured. The results are fairly satisfactory, considering that the necessary conditions of the experiments were not the best for calorimetric measurement. They serve to show, at least, that the continued evolution of heat between $x = 4.8$ and $x = 6$, in Series I, may be accounted for by the action of the 1.2 mol. KOH on the precipitate formed by the 4.8 mol. A previous experiment, made by adding KOH in the calorimeter to the liquid portion of the mixture 1 alum + 5 KOH (the precipitate being removed), gave zero for a result.

Series II.

In the second series of experiments the same quantity of alum was dissolved, 10 mol. KOH added, and the whole made up to 500 cc., as in Series I. To this were added in the calorimeter 500 cc. of sulphuric acid solution containing of H_2SO_4 quantities varying from .5 to 3 molecules. The numerical data are recorded in Table II. It will be seen that the rate of heat disturbance per molecule of H_2SO_4 is practically constant for $n = .5$ and $n = .75$, but increases at $n = 1$; the first precipitation by neutralisation of KOH occurs between $n = .75$ and $n = 1$. The rate then increases to $n = 2.2$, when it again drops. Instead of expressing these direct results graphically, I have calculated from them (at least from Exp. 42–48) the corresponding points in the Lines I and III. The possibility of this calculation will be apparent from considering that H in Series II is the formation heat of potassic sulphate plus or minus the heat disturbance involved in separating the equivalent potassic hydrate from whatever form of combination it may be in before the addition of sulphuric acid. If we assume that the n mol. H_2SO_4 (from $n = 1.5$ to $n = 2.2$) are converted into K_2SO_4, and count the formation heat of the latter as a known quantity, we have the means of calculating indirectly the values of y in Series I for $x = 6$, 7 and 10. These values locate the supplementary Lines II and IV, Plate I. They are separated by a small and approximately constant quantity from Lines I and III.

A similar discussion of the values for $n = .5$ and .75 will make evident whether or not the addition of KOH beyond 8.13 mol. has any effect. The formation heat of K_2SO_4 is, according to Thomsen, 31.288 Cal. One-half of this, 15.644 Cal., is larger by .96 than the mean result of Exp. 36–39, Series II, which would indicate that heat was absorbed in liberating KOH from its pre-

vious state of combination, and hence that the combination of the 9th and 10th mol. in Series I was accompanied by heat evolution. This, if true, would be an interesting fact; but the question arises, May not the formation heat of K_2SO_4 in Exp. 36–39 be less than 31.288 Cal., this value having been determined for a degree of concentration six times as great? I therefore determined it independently, using first the same quantities of KOH and H_2SO_4 as occur in the reaction $n = .5$, and then six times these quantities, the volume 1000 cc. remaining the same throughout. In the last case, the proportion is about the same as in Thomsen's experiment. The data are shown in Table IV. At the degree of concentration which corresponds to Exp. 36-39, the formation heat of $\frac{1}{2}K_2SO_4$ is found to be (Exp. 57–61) 14.63 Cal., which agrees with H in Exp. 36–39; while for one-sixth this dilution H is found to be 31.26 or 15.63 for $\frac{1}{2}K_2SO_4$; Exps. 53 and 54 correspond to Thomsen's conditions.

This proves that the second half of the 9th mol. and the 10th mol. in Series I are not in chemical combination, or, at least, that there is no evidence of it in the thermal phenomena. In other words, the heat disturbance ceases when 8.13 mol. KOH have been added, as indicated in Line I, Plate I.

As dilution was found to affect the determination of the formation heat of K_2SO_4, it became desirable to test its influence upon the resultant H of Series I, in which this formation heat is the principal element. To do this the reaction heat of 6 mol. KOH on 1 of alum was determined, the absolute amount of substance undergoing change in the standard volume, 1000 cc., being only one-fourth the quantity used in Exp. 23–26, Series I. These data are recorded in Table V. The mean result of the five experiments is 29.26 Cal., in place of 30.66 by the previous experiments.

It seems not improbable, in view of these facts, that the tendency of Line III, Plate I, to rise between $x = 1.5$ and $x = 5.1$ may be due to the increase in the amount of substance undergoing change in the unit of volume.

The complexity of the thermochemical results thus far described made evident the necessity of a sharper definition of the chemical changes actually taking place in the calorimeter. The study of these constitutes the second part of this paper.

PART II.

General Method.—It would seem that the most direct method of obtaining evidence as to the exact chemical change would be to determine the composition of the various precipitates produced in the calorimetric experiments. The impossibility, however, of washing them without changing their composition, indicated rather the analysis of the filtrate from them as the preferable method. Either one determines only the total change in the distribution of constituents between the soluble and insoluble portions of the system.

The method pursued was the following: 50 cc. of alum solution, containing five grams of the crystallised salt, were made up to a little less than 125 cc. The required quantity of KOH solution was also made up to about the same volume. These two solutions were then thoroughly mixed, the volume of the mixture made up accurately to 250 cc. (T 20° C.), again well shaken, and thrown upon a dry filter, the filtration being hastened in some instances by using the pump. From the filtrate separate portions of 50 cc. each were taken, in which were made duplicate determinations of SO_3 and Al_2O_3, and in several instances of K_2O. The SO_3 was determined, of course, by precipitation with $BaCl_2$; the Al_2O_3 by precipitation with NH_3; and the K_2O was weighed as sulphate after the removal of Al_2O_3. The proportion of constituents and water is the same as in the calorimetric experiments, the scale being simply reduced to one-fourth.

Analyses somewhat similar have been made by S. U. Pickering[1] of the precipitates obtained from aluminic sulphate by addition of varying quantities of Na_2CO_3. His method was to determine the SO_3 and Al_2O_3 in the precipitate itself after thorough washing, although he recognised the fact that its composition was changed by the operation. This would be a serious objection to the use of this method for the purposes of this investigation, although less so in his experiments undertaken from a different standpoint. Our results, so far as they cover the same points, do not conflict in the general direction of their indications, although quantitatively they differ somewhat.

Mills also has determined simply the amount of Al_2O_3 precipitated from alum solution by varying quantities of Na_2CO_3.[2]

It should be noted that the method of this investigation gives

[1] Chemical News **45**, 121, 133, 146. [2] Journal of Chem. Society [2], **41**, 341.

no evidence as to the degree of hydration of the precipitate: that point I am obliged to pass by.

In the first experiment of this series (Exp. *A*) the method was applied in blank to a solution of alum, no KOH being added. The results obtained were:

Al_2O_3 = .1080 gram.	SO_3 = .3321 gram.
= .1074	= .3326
Mean = .1077	Mean = .3324

As these correspond to 1 gram alum taken, multiplying by 100 converts them into per cents. Correcting for the volume of pipettes and flasks makes them respectively 10.90 and 33.64. Adding to these the determinations of K_2O and H_2O, made by separate experiments, makes the complete analysis of the alum used as follows:

	Found.	Cal.
Al_2O_3	10.90	10.76
SO_3	33.64	33.75
K_2O	9.94	9.93
H_2O	45.64	45.56
	100.12	100.00

It is evident that the difference between the results of *A* and of corresponding results of subsequent experiments in which precipitation does occur, gives the amount of Al_2O_3 and SO_3 in the precipitate. The final results of each experiment are reckoned as parts of Al_2O_3 in 100 parts of anhydrous precipitate, and as parts of Al_2O_3 precipitated out of 100 parts of Al_2O_3 present in the total system. The following is an example of a calculation in full:

	Al_2O_3.	SO_3.
A =	.10766 gram.	.33231
D =	.0689	.31134
Precipitate =	.03876	.02097

$$\text{Anhydrous precipitate} = \frac{.03876 \times 100}{.03876 + .02097} = 64.89 \text{ per cent. } Al_2O_3.$$

$$Al_2O_3 \text{ of precipitate} = \frac{.03876 \times 100}{.10766} = 36.00 \text{ per cent. of total } Al_2O_3.$$

The data of this series of experiments are recorded in Table VI. The quantity of KOH varies, as will be seen, from 1.5 to 8 molecules.

Before discussing the results, I describe another series made to reverse, as it were, the conditions of the former.

Fifty cc. of alum solution were taken as before, and to these ten molecules KOH added, and the whole made up to a little less than 125 cc. Sulphuric acid solution containing quantities of H_2SO_4 proportional to 1.5, 2, 2.5 and 4 molecules, was added, and the mixture brought accurately to 250 cc. (*T* 20° C.), thoroughly shaken, filtered, and the filtrate analysed as usual. The only variation was in Exp. *T*, when 5 mol. HCl were used in place of 2.5 H_2SO_4, and this will be more particularly discussed in a subsequent publication. The data of these experiments are recorded in Table VII.

The calculation of the composition of the precipitate is similar to that in the preceding series, except that account must be taken of the SO_3 added.

In three experiments—viz., *H*, *T*, and *S'''* (in *H* and *T* the total amount of precipitate was at its maximum)—the K_2O in the filtrate was determined. The full calculated amount being found, it was deemed unnecessary to determine it at other points, since it evidently formed no part of the precipitate.

Discussion.—The results of the first two series are graphically expressed in Lines V, VI, VII, and VIII, Plate II. In Line V, $x =$ number of molecules of KOH added, and $y =$ per cent. of total Al_2O_3 found in the precipitate; while in Line VII, $x =$ the same, but $y =$ parts of Al_2O_3 in 100 parts of anhydrous precipitate. Continuing Line V beyond $x = 1.5$ and $x = 8$ toward the axis of x, indicates $x = 1.3$ and $x = 8.13$ as the probable points respectively of initial and final precipitation. The line reaches its maximum at $x = 4.8$, making the precipitation of the Al_2O_3 complete at this point.

Line VII shows that the first precipitate is the least basic, containing only 64 per cent. of Al_2O_3; that from $x = 1.5$ to $x = 4$ there is apparently a slight increase of basicity, but that from $x = 4$ to $x = 4.8$ the increase is more rapid; that between $x = 4.8$ and $x = 6$ the rapidity of change is still greater; that at $x = 6$ it drops back again, leaving a precipitate free of SO_3 at $x = 7$. It will be noticed that $x = 4.8$ and $x = 6$ are salient points in these

lines, as they are in Lines I and III, expressing the thermal phenomena.

The points in Line VI, $x = 5$, 6 and 7, are obtained from Exp. *N*, *O* and *T* by making x the number of molecules of KOH left unneutralised by the H_2SO_4 added. It will be seen that they approximate closely to the corresponding points in Line V, the difference being probably within the limits of experimental error. This evidently means that when the same amount of free KOH is present, the same precipitate is obtained, whether it come from adding KOH to alum, or from neutralising the excess of KOH in the alkaline solution of Al_2O_3 obtained by adding 10 KOH to alum. This result was unexpected, and suggested at once the possibility of a chemical equilibrium existing between the constituents of the soluble and of the insoluble portions of the system. To test this idea, Exp. *P* was made, using 4 mol. H_2SO_4. Assuming that 4 mol. KOH out of the ten added are uncombined with H_2SO_4, the 4 mol. H_2SO_4 now added would neutralise them, leaving an excess of 2 mol. H_2SO_4, and making a system, neglecting the K_2SO_4, constituted of 1 mol. Al_2O_3 and 2 H_2SO_4, the same which we suppose to exist when 2 mol. KOH are added to 1 mol. alum. Putting $x = 2$, therefore, the results of Exp. *P* give the points *P* in Lines VI and VIII which approach at least the corresponding points in V and VII. Regarding this as a further indication of an equilibrium, I varied the experiment in the following manner (Exp. *Q*): The usual 50 cc. of alum solution were taken, 6 mol. KOH added, and the whole made up to 250 cc. Another portion of 50 cc. alum solution was then taken, and made up to nearly 250 cc. The two solutions thus prepared were then mixed, made up to 500 cc., thoroughly shaken, filtered, and portions of 50 cc. taken from the filtrate for analysis, as usual. The total system here is evidently the same in the proportion of its constituents (water included), as would be obtained by mixing 1 mol. alum and 3 mol. KOH in a volume of 250 cc. At the same time, we can calculate from Exp. *I*, Table VII, what would be the composition of the precipitate, assuming that it remained the same as produced by 6 mol. KOH in the first mixture, increased only by the remaining 9.47 per cent. of the total Al_2O_3 of the first portion; the KOH uncombined with H_2SO_4 in that portion taking SO_3 from the second portion of alum, but causing no increase of precipitate, since it is equivalent to only about .14 mol.

KOH. The precipitate thus calculated would contain 50 per cent. of the total Al_2O_3 of the system, and have a composition of 95.29 per cent. Al_2O_3 to 4.71 per cent. of SO_3. This gives the crossed points Q ($x = 3$). But actual analysis of the filtrate gives for the precipitate the results recorded in Q, Table VIII, and the points Q in Lines VI and VIII. This shows that the initial distribution of constituents between the soluble and insoluble portions of the system has changed completely, approaching that obtained by adding to 1 mol. alum 3 mol. KOH. The change in this case consists only in an increase of SO_3 in the precipitate.

Another experiment was then made (Exp. R) by mixing in similar manner (1 alum + 6 KOH) in 250 cc. and (1 alum + 1.5 KOH) in 250 cc.; making a total system equivalent to (1 alum + 3.8 KOH) in 250 cc. Calculating as in Q, from Exps. B and I, the initial composition of this mixed precipitate, and on the assumption that the unneutralised .1 mol. KOH of the 6 mol. KOH is added to the 1.5 mol. in the second portion, we obtain the crossed points R ($x = 3.8$). Analysis of the filtrate, on the other hand, gives the points R ($x = 3.8$) in Lines VI and VIII, which likewise shows a very considerable change in the precipitate, and a close approach to the system obtained by adding 3.8 mol. KOH to 1 mol. alum. In this case the change is more complex than in Q, consisting in the precipitate acquiring both Al_2O_3 and SO_3. In other words, the equilibrium has moved the crossed point R up to the point R in VI, and the crossed point R down to R in VIII.

The results already described indicate unmistakably the existence of the equilibrium; but, to vary the evidence still more, Exps. S′, S″ and S‴ were made, as follows:

Aluminum was dissolved in KOH solution and the KOH exactly neutralised by HCl, independent experiments having proved that the precipitate thus obtained is free of acid. The volume of this mixture having the freshly precipitated hydrate in suspension was brought up to 250 cc. Fifty cc. of alum solution (= 5 grams alum) were then added, the whole made up to 500 cc. and thoroughly mixed. Before filtering, portions of 50 cc. each were withdrawn with a pipette, care being taken to insure the uniform distribution of the suspended precipitate by constant stirring. In these portions the precipitate was redissolved by HCl and the total Al_2O_3 of the system determined. The remainder of the mixture

was filtered as usual, and portions of 50 cc. of its filtrate taken for the usual determinations of SO_3 and Al_2O_3. The differences between the total Al_2O_3 and SO_3 and the Al_2O_3 and SO_3 found in the filtrate give the composition of the precipitate. In S′ the amount of Al_2O_3 added as precipitate was 1.12 times that added as alum, making a proportion of 2.12 mol. Al_2O_3 to 3 mol. SO_3 in 500 cc. of volume; equivalent to 1 Al_2O_3 and 1.4 SO_3 in approximately 250 cc. This, so far as relation between Al_2O_3 and SO_3 is concerned, should be equivalent to 1 alum + 3.2 KOH. Using, therefore, the analytical results of S′, Table VIII, and making $x = 3.2$, we obtain the dotted points S′, Plate II, approximating closely to the values otherwise obtained; whereas had the precipitate remained unchanged, it would have been 100 per cent. Al_2O_3 and contained 52.82 per cent. of the total Al_2O_3. These values are represented by the crossed points S′. The change consists mainly in acquiring SO_3.

Exp. S″ is similar, the only variation being in the quantity of precipitated Al_2O_3 added. The results are shown in the points S″ ($x = 2.5$); whereas the crossed points S″ indicate what would have been the results had the precipitate remained unchanged. Here, too, the change is in acquiring SO_3.

Still another experiment, S‴, was made, varying again the quantity of Al_2O_3 added. The actual results are shown in the points S‴ ($x = 2$), and the initial precipitate in the crossed points S‴. Here it is apparent that the change consists in gaining SO_3 and losing Al_2O_3.

The proof of equilibrium is indubitable, the initial precipitate gaining or losing Al_2O_3 or SO_3 as may be necessary to bring about the characteristic distribution of constituents for the given conditions. It is also apparent that K_2SO_4 plays no part, and may be considered as practically outside the system, since its presence in quantity varying from less than one molecule to more than ten molecules has not disturbed the leading phenomenon.

Another fact may be noted here. The corresponding points in Lines V, VI, VII and VIII, that lie to the right of $x = 5$, approximate closely, probably within the limits of experimental error. To the left of $x = 5$ the divergence is greatest, but the difference in every instance lies on the side of approach to Lines V and VII from the initial points, never going beyond. The probable explanation of this lies in the fact that, in all the

experiments yielding Lines V and VII, also the points of the other lines to the right of $x = 5$, the system in its initial state is homogeneous; while in the remaining experiments, with the single exception of Exp. *P*, it is non-homogeneous (liquid and solid). It is not strange, then, that this non-homogeneity exercises a retarding influence upon the equilibrium. It is rather a matter of surprise that it should not prove more of an obstacle than it does.

Effect of Temperature, Time and Dilution on the Equilibrium.

Temperature often exerts an influence in reactions such as I have been describing, and to test its effect in this instance is the object of the three following experiments, E′, E″ and E‴. In the first place, two successive experiments were made as nearly alike as possible, in order to measure the probable variation in the final results of a single experiment. I give the details in full. The solutions were prepared in the usual manner, 4 mol. KOH being added to 1 mol. alum. The temperature of the room in both experiments was about 23° C., but the contents of flasks before bringing up to standard volume and before taking out portions of 50 cc. were cooled, as in previous experiments, to 20° C. The results were as follows:

	E′.		*E″.*	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
Found in 50 cc. I =	.0174 gram.	.28221	.0159	.28203
II =	.0174	.28210	.0162	.28190
Mean =	.0174	.28216	.0161	.28197

	E′.		*E″.*	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
A =	.10766 gram.	.33231	.10766	.33231
E′ =	.0174	.28216	.0161	.28197
Precipitate =	.09026	.05015	.09156	.05034

Anhydrous precipitate = 64.28 per cent. Al_2O_3 64.52 per cent. Al_2O_3
= 35.72 per cent. SO_3 35.48 per cent. SO_3

Precipitate = 83.84 per cent. of total Al_2O_3 85.05 per cent. of total Al_2O_3.

It will be seen that the SO_3 determinations do not differ appreciably more than the duplicate determinations of SO_3 in the same solution; while the amounts of Al_2O_3 obtained differ by more than a milligram, one part in seventeen. So in another instance, .2893 and .2899 gram SO_3 were obtained in two experiments entirely distinct from the beginning. It would almost seem that the equilibrium was more sharply defined with reference to SO_3 than to Al_2O_3. Yet it should be borne in mind that the amounts of SO_3 actually weighed are always large, .28 gram or more, while the amounts of Al_2O_3 weighed were as low as .01 gram, and hence the experimental determination of SO_3 is less affected by error than that of Al_2O_3.

The final results being dependent on the ratio between differences, small compared with the quantities actually measured, considerable latitude of variation must be allowed.

The experiment was then repeated, *E'''*, the only variation being that, after the flask was filled to 250 cc. (at 21° C.), it was heated to about 50–55° C. for twenty-five minutes, then turned into a large beaker with glass cover and heated fifteen minutes more, and finally boiled two or three minutes. The liquid on the cover was rinsed off with the solution, and the whole thrown while boiling hot upon a dry filter, which was covered during the ten minutes of filtration. The filtrate was then cooled to 20° C., and portions of 50 cc. taken as usual for analysis. The loss of water by evaporation could not have been great, and would not affect the ratio between Al_2O_3 and SO_3. The results were:

	Al_2O_3.	SO_3.
I	.0148	.30473
II	.0148	
Mean	.0148	.30473

This makes a precipitate containing 86.25 per cent. of the total Al_2O_3, with a composition of 77.10 per cent. Al_2O_3 and 22.90 per cent. SO_3. The precipitate at the temperature of boiling has, therefore, lost considerable SO_3, while the ratio of the Al_2O_3 precipitated to the total has not much changed.

Exp. E^{IV}. A second variation was made to test the influence of dilution on the equilibrium, since many of the experiments already described indicate that water plays a part in the reaction besides that of a mere solvent. Alum and KOH in the same

quantity as in E', E'' and E''' were mixed, and the solution made up to 1000 cc., instead of 250, making the absolute quantity in unit of volume one-fourth what it was in the preceding experiments. Of the filtrate, portions of 100 cc. were taken, instead of 50, and the quantities of SO_3 and Al_2O_3 found were multiplied by two in order to make them comparable with the others. The results were:

	Al_2O_3.	SO_3.
I =	.0162	.28570
II =	.0160	.28578
Mean =	.0161	.28574

This indicates a precipitate containing 85.05 per cent. of total Al_2O_3, and of composition 66.29 per cent. Al_2O_3 and 33.71 per cent. SO_3.

Dilution also has tended to diminish SO_3 in the precipitate without changing the proportion of Al_2O_3 precipitated.

Is the equilibrium a function of time also? To answer this, a mixture was prepared (Exp. E^v) at the same time as E', and in precisely the same manner. But, instead of filtering at once, as in E', the mixture was allowed to stand in a closed flask at the temperature of the room for seven days, and then filtered as in E', and the filtrate analysed. The result was:

	Al_2O_3.	SO_3.
I =	.0152	.28210
II =	.0146	.28217
Mean =	.0149	.28214

This makes a precipitate containing 86.12 per cent. of the total Al_2O_3, and in composition 64.89 per cent. Al_2O_3 and 35.11 per cent. SO_3, or practically the same as in E'. Here, too, is to be seen the close agreement in quantity of SO_3 and the greater variation in Al_2O_3.

This experiment was suggested by the fact that the basic filtrates obtained by adding one or more molecules of KOH, and removing the precipitate, yield a second precipitate on standing, the length of time apparently depending on the degree of basicity. This second precipitate is also produced in a few minutes by boiling, or by adding a considerable quantity of water. Exp. E^v is therefore interesting as showing that time does not affect the equilibrium while the original precipitate remains in the system.

Conclusion.

It is clear, from the evidence herein set forth, that in the reaction which has been the subject of investigation we have another instance of chemical equilibrium or mass reaction, and the question at once arises, What is the cause of it? Without attempting to answer this definitely at present, we suggest the probability that it may be due to the progressive dissociation by water of basic compounds of Al_2O_3 and SO_3 on the one hand, and of potassic aluminate on the other. It would appear from Exps. *S'*, *S''* and *S'''*, that $Al_2O_3 . 3\ SO_3$ must itself be partly dissociated in water solution, and it is not improbable that the matter may be still further complicated by the dissociation of another substance formed from the products of decomposition of the first. I hope to obtain definite evidence upon this point, by continuing a line of investigation already begun. That the basic sulphates of alumina are dissociated, is apparently indicated by the fact already cited, that the filtrates in experiments *B* to *H* yield a second precipitate on heating, diluting, or standing some length of time; while the crystallised potassic aluminate to which Fremy assigns the formula, $K_2O . Al_2O_3 . 3H_2O$, decomposes on the addition of water with the separation of aluminic hydrate.

However that may be, it is evident—(1), that the reaction between alum and KOH is not by any means as represented in what may be called the ideal equation cited in the beginning of this paper, but that it is much complicated by secondary reactions which render it entirely unsuitable for the determination of the formation heat of the sulphate and other compounds of alumina, although the numerical error introduced by its use may not be great; and (2), that these secondary reactions are of the nature of chemical equilibriums or mass reactions, the distribution of the constituents of the system about the line of solubility being a function of temperature, volume (*i. e.*, dilution), and total mass of constituents.

TABLE I.

1 Alum + n KOH.

$A = B = 500$. $d = 8.5$. $f = 47655.4$.

No. of Exp.	n.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	$h = H \div n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
1	0.5	16.66	17.275	16.96	.060	2.86	5.72	2.85	5.69
2	0.5	16.4575	17.2225	16.833	.0595	2.84	5.67		
3	1.0	16.6675	17.2925	16.973	.1195	5.70	5.70	5.72	5.72
4	1.0	16.57	17.52	17.037	.1205	5.74	5.74		
5	1.5	16.70	17.0675	16.878	.1695	8.08	5.39	8.09	5.39
6	1.5	16.826	17.73	17.27	.1700	8.10	5.40		
7	2.5	17.02	18.073	17.538	.287	13.68	5.47	13.58	5.43
8	2.5	16.6075	17.04	16.818	.283	13.49	5.39		
9	2.5	16.545	17.40	16.965	.285	13.58	5.43		
10	4.5	17.08	17.93	17.497	.513	24.45	5.43	24.42	5.43
11	4.5	16.525	17.16	16.836	.514	24.50	5.44		
12	4.5	17.44	18.255	17.84	.510	24.31	5.40		
13	4.8	16.18	17.0525	16.609	.5335	25.42	5.30	25.79	5.37
14	4.8	17.2125	17.845	17.522	.548	26.12	5.44		
15	4.8	17.37	18.5775	17.965	.535	25.50	5.31		
16	4.8	16.4325	17.80	17.107	.548	26.12	5.44		
17	5.12	17.03	16.92	16.971	.594	28.31	5.53	28.39	5.55
18	5.12	17.06	17.68	17.363	.5945	28.33	5.53		
19	5.12	16.78	17 75	17.257	.5955	28.38	5.54		
20	5.12	16.17	17.0075	16.581	.599	28.55	5.58		
21	5.5	16.69	17.46	17.068	.632	30.12	5.48	30.14	5.48
22	5.5	16.49	17.35	16.912	.633	30.17	5.49		
23	6.0	19.5825	20.15	19.86	.640	30.49	5.08	30.66	5.11
24	6.0	19.84	20.5075	20.167	.633	30.17	5.03		
25	6.0	16.66	17.84	17.241	.6515	31.05	5.18		
26	6.0	16.6925	17.62	17.148	.6495	30.95	5.16		
27	6.5	16.2375	16.8825	16.553	.647	30.83	4.74	30.83	4.74
28	6.5	16.62	17.895	17.248	.6495	30.95	4.76		
29	6.5	16.445	17.705	17.066	.644	30.69	4.72		
30	7.0	19.15	19.72	19.429	.621	29.59	4.23	29.59	4.23
31	10.0	16.9725	18.01	17.483	.617	29.40	2.94	29.27	2.93
32	10.0	16.46	17.84	17.14	.610	29.07	2.91		
33	10.0	16.62	17.74	17.171	.619	29.50	2.95		
34	10.0	19.26	20.34	19.791	.6115	29.14	2.91		
35	10.0	19.1975	20.21	19.696	.....	29.22	2.92		

TABLE II.

1 Alum + 10 KOH + n H_2SO_4.

$A = B = 500$. $d = 8.5$. $f = 47655.4$.

No. of Exp.	n.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	$h = H + n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
36	.50	19.2575	20.49	19.865	.305	14.54	29.07	14.68	29.36
37	.50	19.41	20.445	19.919	.311	14.82	29.64		
38	.75	17.81	19.14	18.465	.4575	21.80	29.07	21.83	29.10
39	.75	17.8175	19.0075	18.404	.4585	21.85	29.13		
40	1.00	18.19	19.5525	18.862	.628	29.93	29.93	30.05	30.05
41	1.00	18.21	19.725	18.957	.633	30.17	30.17		
42	1.50	17.92	18.305	18.107	.998	47.56	31.71	47.39	31.60
43	1.50	17.9675	18.9375	18.444	.991	47.23	31.49		
44	2.00	17.8975	18.98	18.43	1.340	63.86	31.93	63.55	31.77
45	2.00	19.094	19.65	19.366	1.3415	63.93	31.97		
46	2.00	17.605	19.0375	18.311	1.319	62.86	31.43		
47	2.20	17.82	19.0575	18.43	1.4575	69.46	31.57	69.28	31.49
48	2.20	18.22	18.53	18.37	1.450	69.10	31.41		
49	3.00	17.80	18.665	18.225	1.785	85.07	28.36	85.07	28.36

TABLE III.

(1 Alum + 4.8 KOH) + 1.2 KOH.

$A + d = 1008.5$. $B = 124.96$. $f = 47655.4$.

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	Mean H.
	°	°	°	°	Cal.	Cal.
50	18.08	18.67	18.144	.086	4.10	3.83
51	17.57	17.87	17.602	.073	3.48	
52	17.0475	16.565	16.993	.082	3.91	

TABLE IV.

$2\,KOH + H_2SO_4$. $A = B = 500$. $d = 8.5$.

No. of Exp.	n = grams of H_2SO_4.	T_a.	T_b.	T_m.	T_c.	$H = \frac{T_c \times 1008.5 \times 98.}{n = \text{gram } H_2SO_4}$.	Mean H.
		°	°	°	°	Cal.	Cal.
53	6.8071	17.6925	18.45	18.064	2.1435	31.12	31.26
54	6.8071	17.64	18.9075	18.264	2.1385	31.05	
55	6.227	14.62	15.43	15.018	1.9895	31.58	
56	6.227	15.27	15.96	15.608	1.972	31.30	
57	1.0391	17.1725	19.1275	18.138	.312	29.43	29.26.
58	1.0391	18.30	19.45	18.866	.3065	28.91	
59	1.024	14.1675	14.8950	14.524	.311	29.76	
60	1.024	14.845	15.485	15.158	.307	29.38	
61	1.024	14.31	15.6275	14.959	.301	28.81	

TABLE V.

1 Alum + 6 KOH. $A = B = 500$. $d = 8.5$.

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = \frac{T_c \times 1008.5 \times 948.24.}{5}$	Mean H.
	°	°	°	°	Cal.	Cal.
62	18.76	19.83	19.287	.1505	28.82	29.26
63	19.01	20.07	19.532	.148	28.34	
64	19.13	19.77	19.443	.157	30.06	
65	19.54	19.9075	19.718	.152	29.10	
66	19.9925	20.22	20.101	.1565	29.96	

TABLE VI.—Analyses.

1 Alum + x KOH.

Exp.	x.	Grams Al_2O_3 found in 50 cc. of filtrate.	Grams SO_3 found in 50 cc. of filtrate.	Al_2O_3 in 100 pts. of prec.	SO_3 in 100 pts. of prec.	K_2O in 100 pts. of prec.	Per cent. of total Al_2O_3 in prec.
A	0.	.10766	.33231	0.	0.	0.	0.
B	1.5	.09738	.32651	63.93	36.07	.....	9.55
C	2.0	.08310	.31883	64.56	35.44	.....	22.81
D	2.5	.0689	.31134	64.89	35.11	.....	36.00
E	4.0	.01995	.28588	65.39	34.61	.....	81.47
H	4.79	.0	.28967	71.63	28.37	0.	100.
I	6.0	.0102	.32699	94.82	5.18	.....	90.53
J	6.5	.0294	.32827	96.26	3.74	.....	72.69
K	7.0	.0547	.33174	100.	0.	.....	49.19
L	8.0	.1019	.33231	100.	0.	.....	5.35

TABLE VII.—Analyses.

(1 Alum + 10 KOH) + x H_2SO_4.

Exp.	x.	Grm. Al_2O_3 found in 50 cc. of filtrate.	Grm. SO_3 found in 50 cc. of filtrate.	Al_2O_3 in 100 pts. of prec.	SO_3 in 100 pts. of prec.	K_2O in 100 pts. of prec.	Per cent. of total Al_2O_3 in prec.
N	1.5	.0540	.45788 cal. .45679 found.	100.	0.	.....	49.84
O	2.0	.0119	.50011 cal. .49673 found.	96.59	3.41	.....	88.95
T	2.5	.0	.33231 cal. .29512 found.	74.33	25.67	0.	100.
P	4.0	.0867	.66969 cal. .66036 found.	69.20	30.80	.....	19.47

TABLE VIII.—Analyses.

1 Alum + x KOH.

Exp.	x.	Grm. Al_2O_3 found in 50 cc. of filtrate.	Grm. SO_3 found in 50 cc. of filtrate.	Al_2O_3 in 100 pts. of prec.	SO_3 in 100 pts. of prec.	K_2O in 100 pts. of prec.	Per cent. of total Al_2O_3 in prec.
Q	3.0	.0547	.30898	69.42	30.58	.....	49.19
R	3.8	.0300	.29598	68.13	31.87	.....	72.13
S'	3.2	.0516	.13951	70.11	29.89	.....	54.78
S''	2.5	.0543	.15017	70.33	29.67	.....	41.11
S'''	2.0	.0608	.15835	71.74	28.26	0.	24.57

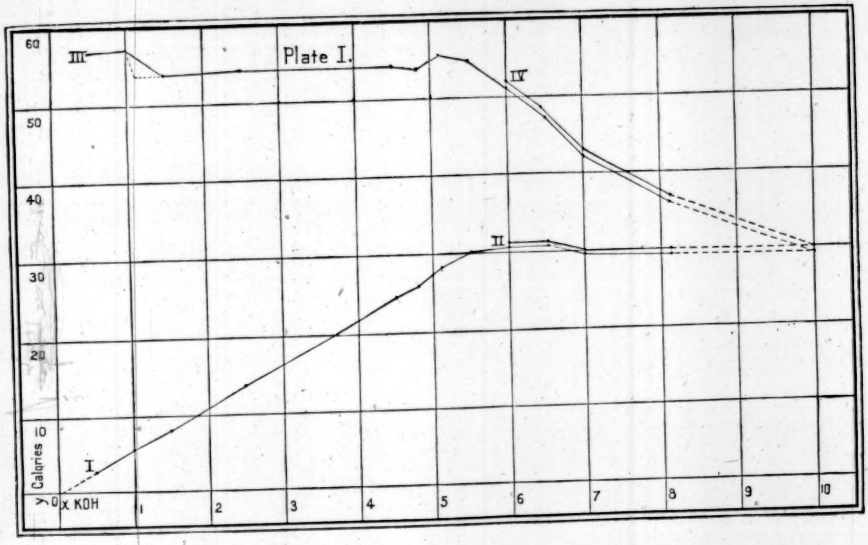


Plate I.
III
IV
II
I
60
50
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30
20
10
0
y Calories
x KOH
1
2
3
4
5
6
7
8
9
10

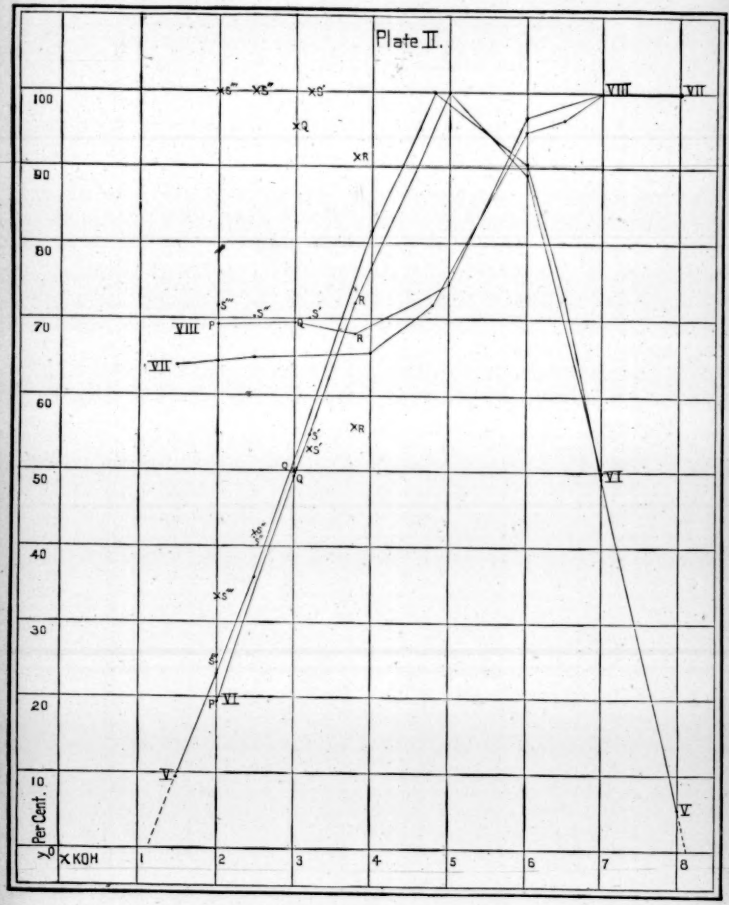


Plate II.
100
90
80
70
60
50
40
30
20
10
0
Per Cent.
KOH
1
2
3
4
5
6
7
8
VIII
VII
VI
V
P
Q
R
S'
S''
S'''

COMPOSITION AND RELATIVE DIGESTIBILITY OF FEEDING-STUFFS.

By E. F. Ladd.

The chemical composition of American feeding-stuffs has, through the efforts of experiment stations and agricultural colleges, been quite thoroughly investigated. But chemical analysis reveals to us only the composition of the fodder—its potency, and not its nutritive value, which can only be known by a knowledge of its digestibility. The mere fact that two substances have nearly the same chemical composition will not warrant us in assuming that they are of like value for feeding. We must know the ease and efficiency of digestibility as well as the chemical composition.

The abundance of natural foods, and the difficulty and expense of experiments for determining the digestibility, have prevented our gaining any extensive knowledge of this subject in America.

Several attempts have been made to determine, by artificial digestion, the nutritive value. Stutzer[1] proposed to determine the digestibility of the albuminoids—the most important compound—by means of the gastric fluid prepared from a hog's stomach, but this is a difficult and tedious task, and not without its faults.

Appreciating the necessity for a better knowledge of American feeds, I set to work analysing and testing their digestibility by the different methods. After much study, and experimenting with Stutzer's method, I instituted a series of experiments, with a solution from scale pepsin as a digestive menstruum, which gave results far above any expectation.

The work accomplished may be found in the Report of the New York Agricultural Experiment Station for 1885; hence, I will only give here a *résumé* of the essential features, with tables of results and a brief consideration of the same.

The Pepsin Method.

A muriatic-acid solution of 0.2 per cent. was prepared and to each litre were added 5 grams of pepsin.[2] Fresh solutions were made for each test. The substance to be digested was thoroughly comminuted as for a chemical analysis. One or two grams were taken, according to richness in nitrogen.

[1] Journal für Landwirthschaft, 1880, p. 195; also Report of Maine State College, 1883.

[2] Scale pepsin from Henry Thayer & Co.

The substance was placed in an Erlenmeyer flask and 150 cc. of the pepsin solution added. Once in two hours 0.1 gram of HCl was added until the solution contained 0.7 gram. The flasks were set in a water-bath heated at from 38° to 42° C. for 14 hours, then allowed to cool down during the night, and on the following day the heating was continued for six hours. They were then filtered, thoroughly washed with water until free from any traces of acid, then with alcohol, and the contents of the filter transferred to a nitrogen flask and dried at 100° C.

The nitrogen in the undigested residue was then determined by Kjeldahl's method.

In Table I are given the analyses of the substances examined. The analyses are given for both dry substances and calculated to actual water contents, but the digestion coefficients are given for the dry substances only.

Tables II and III give the results obtained from the experiments.

In this article the term crude albuminoids applies to $N \times 6.25$, and the true albuminoids were determined by Stutzer's cupric-hydrate method.

Digestion coefficients are given for both crude albuminoids and the true albuminoids.

Notes on Table I.

The first three hays were from the same lot. No. 1[1] as harvested, and in good condition. No. 2 was a sample of the same spread on the ground for one month, exposed to the weather, and selected as an average sample. No. 3 was a sample of the poorest, selected from No. 2, and was somewhat decayed.

No. 4. This was like No. 1, but gave slightly more nitrogen.

No. 5. A portion of No. 4 after having been prepared for analysis, then steamed and redried.

Nos. 13 and 15 were waste products from the American Glucose Co.

No. 14. A similar product from the Glen Cove Starch Co.

Nos. 18 and 19. Selected as fair representatives of the old- and new-process linseed meals.

No. 24. The pea meal used in this test was a sample from the meal fed the cows of Mr. Bronson during the butter test in June, 1885.

No. 22. A sample of corn meal fresh from the mill.

[1] Bulletin No. 6, N. Y. Agl. Exp't Station.

No. 23. Same as No. 22, cooked by boiling with water, then dried and examined.

No. 27. Sample of corn meal having lain in bin fully three months.

No. 28. Same as last, treated as No. 23.

No. 30. No. 29 after remaining in bin until badly heated and somewhat mouldy.

The determinations have all been made in duplicate and only the average given in the following tables.

TABLE No. I.

		Fresh Substances.						Dry Substances.				
	Hay and Coarse Fodders.	Water.	Albuminoids N × 6.25.	Crude fibre.	Nitrogen, free extract.	Fat, ether extract.	Ash.	Albuminoids.	Crude fibre.	Nitrogen, free extract.	Fat, ether extract.	Ash.
1	Clover hay	14.53	11.80	28.22	35.84	3.31	6.30	13.812	33.025	42.113	3.865	7.185
2	Same exposed, average	14.53	10.42	35.14	33.28	2.48	4.15	12.187	41.110	38.953	2.900	4.850
3	Same exposed, poorest	14.53	11.73	34.79	31.79	2.52	4.64	13.843	40.710	37.057	2.960	5.430
4	Clover hay	....	....	....	....	....	....	14.531	...	....	3.86	....
5	Same steamed	....	....	....	....	...	....	14.343	....	....	3.41	....
6	Hay, ordinary, mixed	15.22	5.14	31.28	41.36	2.06	4.94	5.94	36.89	48.91	2.43	5.83
7	Hay, poor, many daisies	16.85	4.91	35.89	35.38	2.09	4.66	5.94	43.16	42.80	2.50	5.60
8	Fodder corn	56.49	3.40	15.46	20.64	1.30	2.71	7.81	35.54	47.44	2.98	6.23
9	Soja hispida	21.23	8.42	22.34	38.29	1.35	8.37	10.69	28.35	48.59	1.75	10.62
10	Ensilage	84.58	1.13	5.01	7.22	1.15	.91	7.31	32.48	46.84	7.45	5.92
	By-Products.											
11	Wheat bran	13.72	13.69	10.52	53.09	2.86	6.12	15.87	12.19	61.53	3.32	7.09
12	Ship stuff	16.00	14.96	4.71	54.12	3.99	6.32	17.81	5.68	64.12	4.87	7.52
13	Gluten meal	8.25	30.16	2.78	52.79	5.16	.86	32.87	3.03	57.54	5.62	.94
14	Starch refuse	63.60	7.66	3.68	20.78	4.04	.24	21.06	10.10	57.08	11.11	.65
15	Starch feed	6.00	16.04	13.02	58.14	6.08	.72	12.50	12.43	65.11	9.45	.51
16	Corn feed, ground germ	8.35	9.85	5.76	62.91	11.21	1.92	10.75	6.26	68.64	12.23	2.10
17	Corn feed, ground hull	6.12	7.04	13.26	64.55	7.53	1.50	7.50	14.12	68.70	8.02	1.60
18	Linseed meal, old process	8.07	31.71	12.31	34.38	8.20	5.33	34.50	13.39	37.40	8.92	5.79
19	Linseed meal, new process	8.55	32.35	13.77	38.13	2.13	5.07	35.37	15.06	41.70	2.33	5.54
20	Cotton-seed meal	18.52	35.21	5.74	21.66	12.32	6.55	43.21	7.31	26.32	15.12	8.04
21	Same cooked	18.52	34.82	....	....	...	....	42.73	....	...	....	....
	Grains.											
22	Corn meal	12.21	10.86	2.24	68.23	5.06	1.40	12.37	2.55	77.78	5.77	1.59
23	Same cooked	12.21	9.88	2.90	69.77	3.85	1.39	11.25	3.31	70.48	4.38	1.58
24	Pea meal	12.08	21.37	11.06	52.02	.86	2.61	24.31	12.58	59.17	.97	2.97
25	Crushed oats	10.09	11.63	16.57	53.98	4.49	3.24	11.87	22.33	58.51	3.90	3.39
26	Corn meal	24.54	8.20	1.52	60.60	3.96	1.18	10.87	2.02	80.31	5.24	1.56
27	Corn meal	8.01	9.61	2.14	73.80	4.98	1.47	10.41	2.33	80.35	5.41	1.50
28	Same cooked	8.01	9.09	2.27	75.80	3.52	1.31	9.87	2.47	82.39	3.85	1.42
29	Corn meal	15.80	10.31	1.58	67.64	3.62	1.05	12.25	1.88	80.33	4.30	1.24
30	Same heated in bin	15.80	9.99	3.88	67.42	1.44	1.57	11.87	4.61	79.03	1.71	1.87
31	Wheat, Clawson's winter	12.80	13.00	3.76	67.40	1.64	1.40	14.93	4.31	77.28	1.88	1.60
32	Bean, navy or pea	12.39	22.17	7.21	53.14	1.38	3.71	25.31	8.23	60.66	1.57	4.23

TABLE No. II.

Digested by Fluid from Hog's Stomach.

No. corresponding to No. of analyses.		Per cent. of crude albuminoids N × 6.25.	Per cent. of true albuminoids.	Per cent. undigested.	Per cent. of crude albuminoids digested.	Per cent. of true albuminoids digested.
1	Clover hay	13.81	10.03	3.62	73.75	63.91
2	Same exposed, average	12.19	9.38	0.20	49.23	33.90
3	Same exposed, poorest	13.84	11.31	7.09	48.76	37.31
26	Corn meal	10.87	8.31	1.71	83.98	79.42
10	Ensilage	7.31	4.46	2.32	68.20	47.98

TABLE No. III.

Digested by Pepsin Solution.

No. corresponding to No. of analyses.	Hay and Coarse Fodders.	Per cent. of crude albuminoids N × 6.25.	Per cent. of true albuminoids.	Per cent. undigested.	Per cent. of crude albuminoids digested.	Per cent. of true albuminoids digested.
4	Clover hay	14.53	10.03	4.70	67.65	53.14
5	Same steamed	14.34	...	0.70	53.27	...
6	Hay, ordinary, mixed	5.94	...	2.09	35.32	...
7	Hay, poor quality, many daisies.	5.94	5.44	2.51	57.69	53.86
8	Fodder corn	7.81	5.88	2.89	63.00	50.83
9	Soja hispida	10.68	9.56	2.57	75.92	73.11
10	Ensilage	7.31	4.56	2.82	61.35	39.25
	By-Products.					
11	Wheat bran	15.87	13.00	2.65	83.27	79.61
13	Gluten meal	32.87	...	5.51	83.23	...
14	Starch refuse	21.06	...	5.00	73.43	...
15	Starch feed	12.50	12.68	4.89	60.80	61.36
16	Corn feed, ground germ	10.75	...	4.54	57.98	...
17	Corn feed, ground hull	7.50	...	2.28	69.71	...
18	Linseed meal, old process	34.50	33.13	3.01	89.52	89.10
19	Linseed meal, new process	35.37	32.19	7.02	78.44	76.33
20	Cotton-seed meal	43.21	40.25	5.30	87.73	86.83
21	Same cooked	42.73	...	11.19	73.81	...
21	Ship stuff	17.81	16.81	2.34	87.86	86.08
	Grains.					
24	Pea meal	24.31	20.19	2.75	88.69	86.38
25	Crushed oats	11.87	10.31	2.15	81.89	79.14
26	Corn meal	10.87	8.31	1.50	86.15	81.95
27	Corn meal	10.41	7.64	2.85	72.58	64.00
28	Same cooked	9.87	7.61	3.64	63.16	52.17
31	Wheat, Clawson's winter	14.93	8.81	1.93	87.07	78.09
29	Corn meal	12.25	8.81	3.57	70.85	59.48
30	Same heated	11.81	8.81	3.58	69.79	59.35
22	Corn meal	12.37	9.41	3.87	68.63	58.87
23	Same cooked	11.25	5.19	4.44	60.53	16.37
32	Bean, navy or pea	25.31	22.06	1.13	95.59	94.93

Of the feeds examined in per cent. of digestibility of the albuminoids, bean meal stands the highest, linseed meal (old process) next, and pea meal but little less, while the mixed hay of rather inferior quality, but similar to much hay fed, stands lowest. The old-process linseed meal shows a higher per cent. of digestibility than the new-process: this difference is due, very likely, to the partial cooking of the meal by steam during the process of oil extraction and preparation of the meal for feed. Cotton-seed meal, much the richest substance examined, gives a high coefficient for digestibility. A marked difference exists between the first three hays, showing plainly the difference between well-cured hay and that exposed to the weather.

Of the raw and cooked foods examined, in every instance the higher digestion coefficients were obtained for the raw foods, and an examination of the table of analyses shows an actual loss in albuminoids by cooking, and a change in the fat rendering it insoluble in ether, and unacted upon by acids or alkalies of the strength used for fibre determinations.

REVIEWS AND REPORTS.

An Account of Recent Researches on Thiophene and its Derivatives.

In December, 1882, Victor Meyer[1] called attention to the fact that there is a difference between the chemical conduct of the purest benzene from coal tar and that from benzoic acid; that while that from coal tar, as shown by Baeyer[2] in 1879, is capable of reacting, in the presence of strong sulphuric acid, upon isatin to form indophenin according to the following equation, as given at that time:

$$C_8H_5NO_2 + C_6H_6 = H_2O + C_{20}H_{13}NO,$$

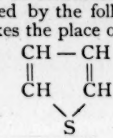
that from benzoic acid effects, under similar conditions, no such change. Meyer forthwith undertook a study of the cause of this difference between these benzenes of different origin. Of a number of hypotheses made at the outset as to the cause in question, the

[1] V. Meyer, Berichte der deutschen chemischen Gesellschaft **15**, 2893. [2] *Ibid.* **12**, 1311.

following one soon proved to be correct—namely, that coal-tar benzene contains two bodies, physically and chemically very similar, one of which is more susceptible to chemical change than the other, and is capable of combining with isatin; when treated with strong sulphuric acid it is converted into the sulphonic acid, while the less susceptible body is unaffected. Coal-tar benzene,[1] when shaken for some time with concentrated sulphuric acid, loses its power of reacting with isatin as described, but the sulphonic acid thus formed, when subjected to dry distillation, gives rise again to benzene, which is active toward isatin.

This fact suggested a method of isolating this new substance so intimately associated with coal-tar benzene. A large quantity, 250 litres, of the purest commercial benzene was vigorously shaken for four hours with 25 litres of strong sulphuric acid; the resulting acid product was neutralised with lead carbonate and then the lead salt, mixed with one-fourth its weight of ammonium chloride, subjected to dry distillation. The product of this distillation contained 70 per cent. of the new body and 30 per cent. benzene. The new substance is obtained pure by again treating the above raw product, diluted with 100 times its volume of ligroin, with strong sulphuric acid, which now does not attack the benzene, and subsequently distilling the lead salt mixed as before with ammonium chloride. This method produces the new substance chemically pure. Thus obtained it forms a colorless, extremely mobile oil, boiling-point 84° (corr.). Analysis established the formula C_4H_4S, which is also in accordance with a determination of its vapor density. Strong sulphuric acid dissolves it in the cold with the greatest ease, but also destroys it completely; hence the necessity of diluting the raw product with an indifferent oil such as ligroin. This conduct towards sulphuric acid and the indophenin reaction with isatin serve as means to detect and identify it. Commercial benzene contains 0.5 per cent. of this substance.

To this new compound Meyer[2] gave the name "thiophene," which shows the presence in it of sulphur, and at the same time indicates the striking similarity which exists between it and its derivatives to the phenyl compounds. The study of a few derivatives, such as the bromine substitution products, the sulphonic acid, amide and chloride, and the carbonic acid, developed the idea that this body must be constituted similarly to benzene, and its structure is represented by the following scheme, in which a bivalent sulphur atom takes the place of two CH groups; thus:



This structure admits the possibility also that thiophene is fur-

[1] V. Meyer, Berichte der deutschen chemischen Gesellschaft **16**, 1465. [2] *Ibid.*, **16**, 1470.

furan C_4H_4O, in which oxygen is replaced by sulphur. The analogy in structure of thiophene, furfuran and pyrrol will be discussed further on in connection with a consideration of certain parallel syntheses of these three bodies.

General Transformations.

Although but a short time has elapsed since the isolation of thiophene, a great many derivatives have been prepared and studied. The rapidity with which these bodies have appeared is not strange, in view not only of the active investigation prosecuted in this extensive and interesting field, but also of the fact that, owing to the great similarity between the thiophene and the benzene series, a number of important general transformations carried out in connection with the latter series have been found equally applicable to thiophene and its homologues.

Quite a long list of chlorine, bromine, iodine, nitro and sulpho derivatives are well known. Perhaps the most important general statements that can be made in regard to them are, in the first place, that they show, with scarcely any exceptions, the indophenin and the Laubenheimer[1] reactions; secondly, they have a surprisingly strong resemblance to the corresponding compounds of the benzene series (this likeness being in some cases so perfect that analysis or the indophenin reaction only will serve as distinguishing means); lastly, they are prepared usually in the same general manner as the analogous benzene compounds.

The chlorine[2] and bromine[3] substitution products are the ready result of treating raw thiophene directly with these elements; the iodine[4] compounds are formed by the action of iodine and mercuric oxide upon crude thiophene. Strong sulphuric acid acts destructively upon undiluted thiophene, but gives rise to well-crystallising and attractive sulphonic acids when its action is modified by dilution with benzene or ligroin.

Concentrated nitric acid[5] acts with destructive and even explosive violence upon pure thiophene; the presence of a negative atom or group in thiophene seems, however, to make it more stable towards oxidising agents and more susceptible to nitration.

Thus iodo-thiophene, by slow and careful treatment with nitric acid, is converted into the iodo-nitro derivative. Also, dibromthiophene is readily transformed into nitro derivatives with less violent action than the iodine product. A great many attempts to obtain nitro-thiophene by the direct action of nitric acid upon pure and also upon diluted thiophene were made in vain, until at last success[6] was attained by passing air laden with thiophene vapor through fuming nitric acid; in this manner mono-nitro- and two isomeric dinitro-thiophenes were prepared. These dinitro com-

[1] V. Meyer, Berichte der deutschen chemischen Gesellschaft **8**, 224. [2] L. Weitz, *ibid.* **17**, 794.
[3] *Ibid.* **16**, 1465. [4] Meyer and Dyson, *ibid.* **17**, 1558. [5] H. Kreis, **17**, 2073.
[6] V. Meyer and O. Stadler, *ibid.* **17**, 2648.

pounds are of particular interest because of the fact that the one melting at the lower point (52°) is transformed, by repeated distillation with water vapor, into the other, which melts at 78°. The lower melting body retains its melting-point even after extensive fractional crystallisation from alcohol, thus indicating that it is a distinct substance.

The reduction[1] of nitro-thiophene to the amido compound offered unexpected difficulties, since it is either entirely unaffected or is decomposed by the action of the reducing agents ordinarily used for this purpose. Success was finally attained, after many vain attempts, by the use of tin and hydrochloric acid in dilute alcoholic solution. The tin double salt $\left.\begin{matrix} C_4H_3SNH_2,HCl \\ C_4H_3SNH_2,HCl \end{matrix}\right\} + SnCl_4$ is by this means obtained, but the free base, thiophenine (amido-thiophene) itself is an exceedingly subtile body which can readily be lost by decomposition, is liable to be overlooked altogether, and is preserved unchanged only by exercise of the greatest care.

The Friedel and Crafts reaction,[2] of such great importance in the aromatic series, is equally applicable to the thiophene series; in the case of thiophene it is unnecessary to use the pure substance, since thiophene is acted upon more readily than benzene; hence crude thiophene (60 per cent. thiophene and 40 per cent. benzene) is employed. By means of this reaction, performed in the usual manner, such interesting bodies as the following have been produced: Phenyl-thienyl-ketone, $C_6H_5-CO-C_4H_3S$; phenyl-thienyl-acetoxime, $C_6H_5-C(NOH)-C_4H_3S$; aceto-thienone,[3] $C_4H_3S-CO-CH_3$; the hydroxylamine derivative of aceto-thienone, thienyl-methyl-acetoxime, $C_4H_3SC(NOH)CH_3$; the phenyl-hydrazine derivative of aceto-thienone, $C_4H_3SC<\begin{matrix} CH_3 \\ N-NHC_6H_5 \end{matrix}$, etc.

Baeyer's reaction, according to which condensation products are obtained by means of aldehydes and alcohols with benzene, takes place in an entirely analogous manner with thiophene;[4] thus, just as Baeyer obtained diphenyl-trichlor-ethane from chloral and benzene through the agency of sulphuric acid, so dithienyl-trichlor-ethane, $CCl_3-CH<\begin{matrix} C_4H_3S \\ C_4H_3S \end{matrix}$ is obtained from thiophene and chloral. Dithienyl-dichlor-ethylene, $CCl_2=C<\begin{matrix} C_4H_3S \\ C_4H_3S \end{matrix}$, phenyl-thienyl-methane, $CH_3<\begin{matrix} C_6H_5 \\ C_4H_3S \end{matrix}$, and a number of other interesting bodies of this class, are known.

The Würtz-Fittig synthesis, by means of which higher members of the benzene series are produced, applied to thiophene[5] in exactly the same general manner as to benzene, yields homologues of thiophene.

[1] O. Stadler, Berichte der deutschen chemischen Gesellschaft **18**, 1490.
[2] A. Comey, *ibid.* **17**, 790. [3] A. Peter, *ibid.* **17**, 2643. [4] A. Peter, *ibid.* **17**, 1341.
[5] Meyer and Kreis, *ibid.* **17**, 1558.

Mono-iodo-thiophene was used in these syntheses in preference to the corresponding bromine compound because of its more ready preparation; thus ethyl-thiophene was prepared according to the following equation:

$$C_4H_3IS + C_2H_5Br + Na_2 = NaBr + NaI + C_4H_3SC_2H_5.$$

In this way the following homologues have been prepared: Methyl-thiophene (thiotolene), $C_4H_3S - CH_3$; ethyl-thiophene, $C_4H_3S - C_2H_5$; normal propyl-thiophene, $C_4H_3S - C_3H_7$; normal butyl-thiophene, $C_4H_3S - C_4H_9$. The boiling-points of these bodies are almost identical with those of the corresponding benzene homologues.

The formation of diphenyl, $C_6H_5 - C_6H_5$, by conducting benzene through a tube heated to bright redness, finds its perfect analogy in the production of dithienyl,[1] $C_4H_3S - C_4H_3S$, by passing pure thiophene through a tube heated only to dull redness; a higher temperature than this causes thiophene to break up with formation of sulphuretted hydrogen and carbon.

The transformation of thiophene-sulphonic[2] acid, $C_4H_3S - SO_3H$, into the carbonic acid according to the method of Merz (by distillation of the potassium salt with potassium cyanide) takes place readily. By this reaction thiophene-nitrile, $C_4H_3S - CN$, is obtained, but the yield of this body is very decidedly less than that of benzene-nitrile in the analogous transformation of benzene-sulphonic acid. The conversion of the nitrile into the carbonic acid is effected in the usual manner, yielding the mono-carbonic acid (thiophenic acid), $C_4H_3SCO_2H$, the similarity of which to benzoic acid is simply astonishing.

The Würtz synthesis of benzoic acid from a halogen substitution product of benzene and the ethyl ester of chlor-carbonic acid, readily yields a thiophenic acid[3] according to the following equation:

$$C_4H_3SI + ClCOOC_2H_5 + 2Na = NaCl + NaI + C_4H_3SCO_2C_2H_5.$$

Structure of Thiophene.

The question, "What is the probable structure of thiophene?" is naturally at present one of the greatest interest. It has already been stated that Meyer proposed, almost at the beginning of the investigations in this field, a scheme which was based chiefly upon the marked resemblance which exists between thiophene, with the few derivatives at that time studied, and the benzene series. This structure, although of course suggested by and in accordance with the comparatively few facts at hand, was considered by its author as worthy of discussion, and valuable as a working hypothesis. The establishment of the structure of thiophene is certainly a task no more readily to be accomplished than the proof of the constitu-

[1] R. Nahnsen, Berichte der deutschen chemischen Gesellschaft **17**, 789.
[2] Meyer and Kreis, *ibid.* **16**, 2172. [3] R. Nahnsen, *ibid.* **17**, 2192.

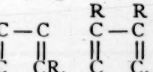
tion of benzene, which, even after years of investigation, can hardly be regarded as furnished.

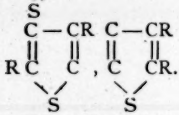
In considering the probability of the structure[1] proposed for thiophene—*i. e.*, as represented in the following scheme,

questions in regard to the following points at once present themselves: the number of isomeric substitution products; formation o addition products; the position of the sulphur atom; the conduct of thiophene when oxidised, and the product thus formed; and, finally, the production of thiophene synthetically from substances of known composition. A not inconsiderable amount of valuable evidence upon a number of these points has already been accumulated, and although a few cases of what seems to be physical rather than chemical isomerism remain to be perfectly explained, still the scheme is in accordance with the facts known at present.

An inspection of this scheme shows that two mono-substitution products are theoretically possible—namely,

; four di-substitution products,



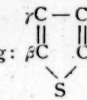


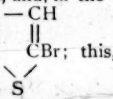
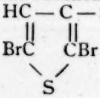
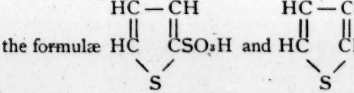
The carbon atoms in this scheme were originally designated thus:

but since it was afterwards found that a number of compounds designated α were *chemically*, but not *physically*, identical with the β-compounds, and that the latter are really to be represented thus:

the original lettering of the carbon

[1] Meyer, Berichte der deutschen chemischen Gesellschaft **18**, 596.

atoms was changed to the following:  , the letter α being retained to designate the physical isomers, and having therefore no place in the structural scheme.

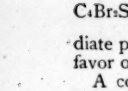
One of the first investigations[2] having for its object a study of the isomeric mono-substitution products was upon the sulphonic acids; one of these was prepared by direct treatment of thiophene with sulphuric acid; the other was obtained by introducing the sulpho group into dibrom-thiophene, and afterwards extracting the bromine by means of nascent hydrogen.[3] The position of the bromine atoms was not actually known, but it was assumed, on account of the perfect analogy which exists between thiophene and benzene in regard to substitution, that in thiophene as in benzene the two bromine atoms substitute the hydrogen atoms of those places which are separated by the greatest number of carbon atoms—*i. e.*, giving rise to para-dibrom-benzene, and, in the case of thiophene, to the following compound:  ; this, by introduction of the sulpho group, would become:  , which, by extraction of bromine, is converted into . The two sulphonic acids produced in these different ways proved to be isomeric, and are then represented by the formulæ  .

In the course of this investigation another body of interesting properties was produced—namely, dibrom-disulpho-thiophene, ; this gives a well-characterised anhydride:

[1] Gattermann, Kaiser and Meyer, Ber. der deutsch. chem. Gesellschaft **18**, 3011.
[2] J. Langer, *ibid.* **17**, 1566. [3] Meyer, *loc. cit.*

$C_4Br_2S\begin{cases}SO_2\\SO_2\end{cases}>O$,[1] which fact is an argument in favor of the immediate proximity to each other of the sulpho groups, and hence in favor of the above structural formula.

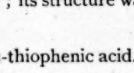
A consideration of the thiophenic (mono-carbonic) acids is of interest, because it presents what seems to be an example of physical[2] rather than chemical isomerism, as yet not explained. As already stated, a thiophenic acid was first formed by converting a salt of the sulphonic acid by Merz's synthesis into the carbonic acid; this acid melts at 118°; its structure was believed to be the following:



$HC-CH$ ‖ ‖ $HC \quad C-CO_2H$, α-thiophenic acid.[3] Later, mono-iodo-thiophene was converted into a carbonic acid[4] by means of the Würtz synthesis; thus:

$$C_4H_3SI + ClCO_2C_2H_5 + 2Na = NaI + NaCl + C_4H_3SCO_2C_2H_5.$$

The acid thus obtained had different properties from the one from the sulphonic acid, its melting-point being 129°, and to it, therefore,



was ascribed the structure, $HC-C-CO_2H$ ‖ ‖ $HC \quad CH$, β-thiophenic acid.

A *third* thiophenic acid[5] was afterwards prepared by oxidising a methyl-thiophene, $C_4H_3S-CH_3$, which was the synthetical result of the action of phosphorus trisulphide upon sodium pyrotartrate; to this acid the name γ-thiophenic acid[6] was given. Not only was thus a third thiophenic acid prepared, but the synthetical methyl-thiophene[7] which produced it was also different from the two methyl-thiophenes already known; this was shown by the fact that the third methyl-thiophene yields a tribrom-methyl-thiophene different from the two already known. It is evident, then, that while Meyer's proposed structural scheme admits only two isomeric mono substitution products of thiophene, three methyl-thiophenes, three thiophenic acids, and also three tribrom-methyl-thiophenes, actually exist, while only two tribrom-methyl-thiophenes are possible according to the scheme.

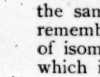
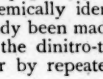
These three apparent contradictions of Meyer's views in regard to the structure of thiophene have, however, been explained as follows:

The α- and β-thiophenic acids were converted into the dibrom-derivatives, $C_4HBr_2CO_2H$;[8] the α-derivative was obtained from

[1] Berichte der deutschen chemischen Gesellschaft **17**, 1569.
[2] Meyer and Kreis, *ibid.* **16**, 2172.
[3] Volhard and Erdmann, *ibid.* **18**, 454.
[4] Nahnsen, *ibid.* **17**, 2192.
[5] Volhard and Erdmann, *loc. cit.*
[6] F. Muhlert, *ibid.* **18**, 1770, 3003.
[7] Meyer, *ibid.* **18**, 3008.
[8] A. Peter, *ibid.* **18**, 542.

the sulphonic acid resulting from direct treatment of thiophene with sulphuric acid; the β-derivative was obtained by oxidation of aceto-thienone, $C_4H_3S.CO.CH_3$, and treatment of the resulting carbonic acid with bromine. At first[1] the α-dibrom-thiophenic acid showed the melting-point 212°–213°, but, when re-obtained after conversion into the amide or the methyl ester, it showed a higher melting-point, 220°–221°, which is that of the β-acid; the amides and methyl esters were identical. It was further found[2] that dry distillation of the calcium salts of α- and β-thiophenic acid results in the formation of the same thienone, $C_4H_3S—CO—C_4H_3S$.

It was therefore concluded[3] that, although α- and β-thiophenic acids are unquestionably different physically, since they furnish the same derivatives, they are chemically identical. (It will be remembered that mention has already been made of a similar kind of isomerism in connection with the dinitro-thiophenes, one of which is converted into the other by repeated distillation with water vapor.)

One of these thiophenic acids, β, is believed to have the composition  , the other, γ, the composition  , while the α, physically different from, but chemically identical with, β, is not of course specially designated in the structural scheme.

The apparent isomerism of three thiotolenes was accounted for by the discovery that thiotolene (methyl-thiophene) from coal tar is a mixture of the β- and γ-varieties, as proved by the fact that if a mixture of two parts of γ- to five parts of β-thiotolene be converted into tribrom-thiotolene, this latter compound is identical with that obtained from coal-tar thiotolene. This tribrom-thiotolene must then be a mixture of the β- and γ-products, but it has the peculiar property of not breaking up into its component bodies even by repeated crystallisations.

No facts, therefore, in view of these explanations, in regard to mono substitution products of thiophene, are at variance with Meyer's proposed structure.

It is interesting to note in regard to thiophene-dicarbonic acid, $C_4H_2S\!<\!\begin{matrix}CO_2H\\CO_2H\end{matrix}$, that, although it has been prepared in five different ways, but one of the four theoretically possible isomers has as yet been obtained. The five different methods employed are as follows: From thiophene-disulphonic acid, from thioxene $C_4H_2S\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ by oxidation, from aceto-methyl-thienone by oxidation, from iodo-ethyl-thiophene, and from aceto-ethyl-thienone.

[1] R. Bonz, Berichte der deutschen chemischen Gesellschaft **18**, 2308.
[2] L. Gattermann, *ibid.* **18**, 3014. [3] Gattermann, Kaiser and Meyer, *loc. cit.*
[4] E. Schleicher, **18**, 3015, and also J. Rosenberg, *ibid.* **18**, 3031.

Syntheses of Thiophene and Homologues.

The syntheses of thiophene and its homologues thus far effected are of exceeding interest, not only in regard to the light thereby thrown upon the question of structure, but also because of the relation which they have shown to exist between thiophene, furfuran and pyrrol.

Ethyl sulphide $(C_2H_5)_2S$, when conducted through a red-hot tube, gives rise to a liquid which shows the indophenin reaction.[1]

Ethylene, illuminating gas or ligroin vapors conducted over heated pyrites, give thiophene.

The color reactions obtained from the product of boiling crotonic acid with phosphorus sulphide indicated the production of thiophene. Normal butyric acid conducts itself similarly, but not so with isobutyric acid, whose composition, moreover, is not such as to indicate the possibility of yielding thiophene according to the proposed thiophene structure. Other syntheses of thiophene are of more value as indicating the structure of this substance.

C. Paal[2] has performed a number of very instructive syntheses in the furfuran, pyrrol and thiophene series, which are valuable as showing the high probability of a similar constitution in these bodies. The substance known as aceto-phenone-acetone, $C_6H_5CO-CH_2CH_2COCH_3$, when treated with substances capable of abstracting water, yields phenyl-methyl-furfuran, and the transformation is thus explained: In an intermediate stage of the transformation this substance passes into an unsaturated alcohol, and from this a molecule of water is given off as follows:

$$C_6H_5COCH_2CH_2COCH_3 = C_6H_5C.OH-CH.CH$$

$$-C.OH-CH_3 = C_6H_5.C \quad \begin{matrix} CH-CH \\ \| \quad \| \\ C.CH_3 \end{matrix} + H_2O.[3]$$

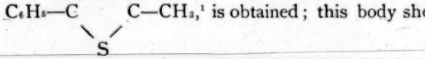
$$\quad\quad\quad

By heating aceto-phenone-acetone with phosphorus pentasulphide in a sealed tube to 120–130° for half an hour, 60 to 70 per cent. of the theoretical yield of phenyl-methyl-thiophene,

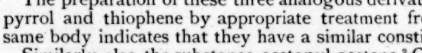
is obtained; this body shows the characteristic reactions of the thiophene series with isatin and phenanthrene-quinone.

The preparation of these three analogous derivatives of furfuran, pyrrol and thiophene by appropriate treatment from one and the same body indicates that they have a similar constitution.

Similarly, also, the substance, acetonyl-acetone,[2] $CH_3COCH_2CH_2COCH_3$, when treated with phosphorus tri- or pentasulphide, yields a thiophene derivative—namely thioxene (dimethyl-thiophene); thus:

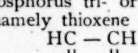


The same body treated with alcoholic ammonia yields dimethyl-pyrrol; thus:



The thioxene obtained as above showed great similarity to thioxene from coal tar, although it could not be affirmed with certainty that the two are identical.

Replacement[3] of phosphorus sulphide by phosphorus selenide gave the interesting substance seleneoxene,



in which selenium replaces the sulphur of thioxene; this selenium compound shows the isatin and phenanthrene-quinone color reactions.

Another synthesis was effected from mucic acid.[4] This substance by distillation, as is well known, yields a furfuran derivative, but if its ammonium salt be heated, it passes into pyrrol. These facts suggested the idea that by the action of hydrogen sulphide a thiophene derivative could be produced. After a number of attempts to realise this synthesis, success was attained by the action of barium sulphide upon mucic acid, producing a mono-carbonic acid of thiophene identical with that obtained by Nahnsen from iodo-thiophene. The reaction is thus explained:

[1] Berichte der deutschen chemischen Gesellschaft **18**, 369. [2] *Ibid.* **18**, 2251.
[3] *Ibid.* **18**, 2255. [4] Paal and Tafel, **18**, 456.

(I.) $CO_2H.CHOH.CHOH.CHOH.CHOH.CO_2H + BaS = \begin{matrix}CO_2ba\\|\\(CHOH)_4\\|\\CO_2ba\end{matrix} + H_2S.$

(II.) $\begin{matrix}CO_2ba\\|\\(CHOH)_4\\|\\CO_2ba\end{matrix} + H_2S = baO_2C.C\begin{matrix}CH-CH\\\|\quad\|\\S\end{matrix}C.CO_2ba + 4H_2O.$

(III.) $2.\ baO_2C.C\begin{matrix}CH-CH\\\|\quad\|\\S\end{matrix}C.CO_2ba + Ba(OH)_2 = 2\begin{matrix}CH-CH\\\|\quad\|\\CH\quad C\\\diagdown\ \diagup\\S\end{matrix}C.CO_2ba + 2BaCO_3.$

By distillation of the calcium salt of this acid, thiophene identical in every respect with thiophene from coal tar was obtained.

The interest and the importance of this synthesis are apparent, since, the constitution of mucic acid being known, the position of the carboxyl group in the thiophenic acid formed from it is at once determined as being that adjoining the sulphur atom, or which is now designated as the β-position.

Volhard and Erdmann[1] have also effected a synthesis of thiophene by heating a mixture of succinic anhydride and phosphorus pentasulphide. The thiophene produced is identical with that from coal tar.

Also, by treatment of sodium pyrotartrate with phosphorus trisulphide, the same authors have produced a thiotolene (methylthiophene) from which by oxidation was derived the γ-thiophenic acid already referred to.

The thiophene homologues, thiotolene,[2] $C_4H_3S{-}CH_3$, and thioxene,[3] $C_4H_3S{<}\begin{matrix}CH_3\\CH_3\end{matrix}$, have been obtained from commercial toluene and xylene, both of which were expected to contain these substances, since they show the Laubenheimer reaction.

As has already been shown, coal-tar thiotolene is a mixture of the β- and γ-isomers. Coal-tar thioxene has been proved by Paal's synthesis to be a β-dimethyl-thiophene.

Investigations having for their object the extraction of other higher homologues of thiophene from the analogous commercial benzene homologues are in progress. W. C. Day.

[1] Berichte der deutschen chemischen Gesellschaft **18**, 454.
[2] Meyer and Kreis, *ibid.* **17**, 788, 1558; K. Egli, **18**, 544; Meyer, **18**, 1326.
[3] K. Schulze, **17**, 2852; J. Messinger, **18**, 563, 1636, 2300.

Valuation of Commercial Phosphates.

An Agreement arrived at between the Chemists of the Experimental Stations and the Manure Manufacturers of South Germany, upon a New Basis for Establishing the Commercial Value of Superphosphate and Precipitated Phosphate.[1]

For the last twenty years the need has been felt for establishing a basis for determining the commercial value of phosphatic manures other than that dependent upon the amount of total and soluble phosphoric acid which they contain. Superphosphates made from such phosphates as Lahn phosphorite have, in consequence of their containing so-called "reverted" phosphate, a higher agricultural value than that indicated by the amount of phosphoric acid soluble in water which they contain; and since phosphatic manures consisting exclusively of precipitated phosphates insoluble in water have lately been brought in increasing quantities into the market, the need for some other basis for valuing manures has become more and more pressing.

R. Fresenius, in conjunction with Neubauer and Luck, found, as is well known, in neutral ammonium citrate, a salt which in solution of a suitable strength, and at a given temperature and time for extraction, proved serviceable enough for separating the precipitated phosphates from that portion of phosphorite superphosphate insoluble in water. This method, however, did not satisfy the requirements of the manure trade, inasmuch as the manurial value of this (reverted) phosphoric acid compared to that of phosphoric acid soluble in water was unknown. In order to solve this question, Petermann and Grandeau carried out some experiments, from the results of which they concluded that phosphoric acid soluble in citrate was of the same value as phosphoric acid soluble in water. This, however, was disputed in Germany, and the joint meeting of agriculturists and chemists held at Karlsruhe, in the year 1879, passed the following resolution:

"This meeting recognises the value of reverted phosphate for certain kinds of soil, and is in no way opposed to its determination, if required by the agriculturist or manufacturer, but considers that the experiments hitherto made do not furnish evidence sufficient to establish a valuation of reverted and precipitated phosphates."

Field experiments were now carried out, whilst at the same time a method was sought for to effect the determination of phosphoric acid soluble in the soil. Of the field experiments on the value of reverted and precipitated phosphates one has gradually become tired: they led to no issue, and it was impossible that they could do so. They have again been abandoned. Attempts to find a means, by merely laboratory operations, of determining phosphoric acid "soluble in the soil" have also proved fruitless, and it was indeed scarcely possible that they could succeed, since the very expression "phos-

[1] Translated and contributed to the Chemical News by H. H. B. Shepherd. From Chemiker Zeitung, 1886, **10**, 1, 2, 3.

phoric acid soluble in the soil" conveys no precise meaning, and, moreover, the means employed for this end could not themselves be held free from objection.

Ammonium citrate, it has been urged, is an entirely unsuitable material for determining phosphoric acid "soluble in the soil," as it dissolves only insignificant quantities of phosphoric acid out of Peruvian guano, bone-meal and other similar manures which experience has shown contain much effective phosphoric acid. Free 1 per cent. citric acid, on the other hand, has been recommended as being far better, since it not only dissolves precipitated phosphate quite as well as does ammonium citrate, but it also takes up some 70 or 80 per cent. of the phosphoric acid contained in bone-meal and raw Peruvian guano, and shows besides that ground raw phosphorite contains about 4 per cent. of phosphoric acid soluble in the soil, which at any rate is correct, "for no agricultural chemist doubts that ground raw phosphorite used in large quantities *does* produce a certain amount of effect."

My own experiments have shown, however, that the manurial value of phosphoric acid soluble in 1 per cent. citric acid varies, according as it is presented to the plants in the form of precipitated phosphate of lime, washed-out high-class superphosphate, or finely ground phosphate. Supposing the manurial value of the phosphoric acid soluble in 1 per cent. citric acid to be represented by 100 in the case of precipitated phosphate of lime, its value in the case of washed-out high-class superphosphate would be represented by 160_4 and in the case of finely ground raw phosphorite by 2. Citric acid is therefore not a suitable means for dissolving out phosphoric acid from the different commercial phosphates in a manner that will compare with that effected by the soil and the roots of plants.

In addition, however, to ammonium citrate and free citric acid, potassium oxalate has been proposed as a menstruum, thus showing to what precision the whole question has shaped itself in the practice of the manure trade! Besides phosphoric acid soluble in water, the agriculturist can purchase now-a-days reverted phosphoric acid, phosphoric acid soluble in the soil, soluble in citrate or in citric acid, root-soluble, half-soluble, and precipitated-assimilable phosphoric acid; and he can have his analyses made by the methods of either Fresenius, Petermann, Halle (18th December, 1881), Tollens-Stutzer, or Liebig, or by the Anglo-Continental method; and if the agriculturist enquires what value is to be attached to these many-styled forms of phosphoric acid, he is told that this is not yet accurately known.

For some years I have been endeavoring to establish the groundwork necessary to throw some light upon this confused state of matters, and I proceeded upon the following lines: If the agriculturist be offered pure superphosphate of lime, it ought to be no difficult matter for him to obtain an opinion upon its value. If the

manure merchant's price for phosphoric acid soluble in water averages about 58 pf. per kilo., the farmer knows that he will be right in paying 11 marks 60 pf. per 100 kilos. for a superphosphate containing 20 per cent. of phosphoric acid soluble in water. It is different, however, in the case of high-class and phosphorite superphosphates or precipitated phosphate. The buyer has then no idea in what relation the value of the precipitated phosphoric acid stands to soluble phosphoric acid of pure superphosphate of lime. If such manures are to be freely salable, one should be able to inform the agriculturist positively what percentage of phosphoric acid equal in manurial value to phosphoric acid soluble in water is contained therein. If this could be done, the buyer would be in a position to tell exactly how much he could afford to pay for the manure, and how it should compare as regards cost with pure superphosphate of lime. For the requirements of the manure trade, therefore, an analytical method is wanted which will give the phosphoric acid of phosphorite superphosphate, of high-class superphosphate, and of precipitated phosphate in their equivalents of phosphoric acid soluble in water, a method which will show how much per cent. of phosphoric acid of the manurial value of phosphoric acid soluble in water is present, or, in other words, the manurial value of the material expressed in terms of phosphoric acid soluble in water. Or, if we call such phosphoric acid simply "soluble" phosphoric acid, and agree that by this term we are to understand phosphoric acid of the same manurial value as phosphoric acid soluble in water, then the question presents itself as follows:

1. By means of manurial experiments to fix the relative manurial values of certain phosphatic manures expressed in terms of "soluble" phosphoric acid—*i. e.*, in terms of phosphoric acid of the same manurial value as phosphoric acid soluble in water.

2. To find an analytical method which shall furnish results agreeing exactly with the percentage of "soluble" phosphoric acid obtained by the manurial experiments.

This question has been my study during a long series of years. As regards the carrying out of my experiments, however, and the details which had to be taken into consideration, I must here confine myself to merely cursory references.

The manures which I used were the following:

1. Pure superphosphate of lime.
2. A commercial precipitated phosphate of lime, prepared by precipitation in a strongly acid solution, and termed dicalcium phosphate.
3. A commercial precipitated phosphate of lime, precipitated with excess of lime, and termed tricalcium phosphate.
4. A washed-out high-class superphosphate.
5. A washed-out phosphorite superphosphate.
6. Finely ground raw phosphorite.

I thought it unnecessary to include also the superphosphates 4 and 5 in the original unwashed-out condition, as, in the presence of so overwhelming an amount of phosphoric acid soluble in water, the effect of the precipitated phosphate contained in them would not have been sufficiently marked. The washing-out of the superphosphates was itself a matter for careful consideration, inasmuch as variations, both qualitative and quantitative, in the precipitated phosphoric acid, arise according as the wash-water at first poured upon the superphosphate is allowed to filter faster or slower through the mass. The quantity of the wash-water used and the length of time occupied by the washing have also their influence, and the variations thus caused would be sufficient to affect the results of the manurial experiments to such a degree as to render the carrying of them out in practical working inadmissible. In the examination of this question I now started with the following consideration: It is necessary in superphosphates to distinguish between—

1. The phosphoric acid which goes into solution on treating 20 grams of superphosphate with 1 litre of water for two hours; and,

2. The phosphoric acid which remains undissolved in the residue.

The manurial value of the phosphoric acid referred to under 2 must be obtained by means of manurial experiments, and a suitable material for such experiments can be prepared by digesting 20 grams of superphosphate in 1 litre of water, or 200 grams in 10 litres, for two hours, with frequent shaking, collecting the residue upon a filter, and, without further washing, allowing it to dry at the ordinary temperature of the air. In this way I produced the so-called washed-out superphosphates. I must further remark that I carried out the experiments in zinc vessels holding about 16 kilos. of earth, and that I experimented upon three kinds of soil—viz., sandy soil poor in lime, loamy soil containing lime, and Rhenish-Hessian soil rich in line. The moisture in the soil was kept as constant as possible, and at about the medium percentage (10 to 15). The crops upon which I experimented were barley, oats, peas and grass.

I have already frequently expressed myself concerning the peculiarities of the results obtained by my method, but I now briefly communicate the following:

1. The phosphoric acid found in bicalcium phosphate by the Fresenius method proved equal in value to 100 per cent. of phosphoric acid soluble in water.

2. The phosphoric acid found in the tricalcium phosphate by the Fresenius method proved equal in value to 75 per cent. of phosphoric acid soluble in water.

3. The phosphoric acid found in the washed-out high-class superphosphate and phosphorite superphosphate by the Fresenius method proved, on the average, equal in value to 70 per cent. of phosphoric acid soluble in water.

I must here remark that these data have reference to the action

which the phosphates, applied in the spring at seed-time, exercised on the crops; the so-called "after-effects" of the phosphates are therefore left out of consideration. Arrangements for carrying out the experiments so as to show indubitably the after-effects of the manures have only been at my disposal since the beginning of the year 1885, and I have naturally not been able to bring the work in connection with them to a conclusion.

4. The results of the manurial experiments give the following percentages of "soluble" phosphoric acid—*i. e.*, of phosphoric acid equal in value to phosphoric acid soluble in water—contained in the manures used:

	"Soluble" phos. acid.
Bicalcium phosphate, ...	30.6 per cent.
Tricalcium "	16.4
Washed-out high-class superphosphate, . .	17.9
Washed-out phosphorite superphosphate, .	3.0
Finely ground raw phosphorite, . . .	0.1

Having obtained these results, the first part of my task was accomplished. In five different phosphatic manures the percentages of "soluble" phosphoric acid was obtained, and it still remained to find a menstruum which under the same circumstances would dissolve phosphoric acid out of each manure in the above proportions—that is to say, 30.6 per cent. out of bicalcium phosphate, 16.4 per cent. out of tricalcium phosphate, and 17.9 per cent. out of washed-out high-class superphosphate.

After many experiments with all possible organic acids I arrived at the same conclusion as Tollens and Stutzer—viz., that of all organic acids, citric alone can be considered admissible; but even this acid, or at any rate the exclusive use of it, proved unsuitable, since its action upon phosphate of iron and alumina is too weak in comparison with its action upon phosphate of lime. I therefore made experiments with its ammonium salts, and came to the same opinion as Fresenius—viz., that of all salts of citric acid, only the ammonium citrate can be considered available. It followed from this that in a suitable mixture of neutral ammonium citrate and free citric acid the properties of both would combine to form a solvent available for the various phosphates. A few preliminary experiments confirmed this supposition.

Now that the preliminaries of the required method had been decided upon, I determined to take into consideration the details of the process and all the practical requirements necessary for a method intended to further the object in view.

I essentially kept in mind the following considerations:

1. The method must allow of superphosphate being treated directly—*i. e.*, without having first to remove the phosphoric acid soluble in water.

2. In order that there may be no difficulty in obtaining a representative sample, sufficient of the material under examination must be taken for extraction (at least 5 grams per ½ litre).

3. The length of time to be decided upon for the extraction must be such that in the event of 30 or 40 superphosphates being in hand at once they can be dealt with without inconvenience. The longer the time agreed upon for extraction, the less likely can any deviations from such time affect the results; and provided it be observed within an hour one way or the other, I recommend as most convenient that the period for extraction be from one day to the next.

4. Also the prescribed degree of temperature must be such as to render its maintenance easily controlled, so that deviations may not lead to differences. The so-called temperature of the room, 13° to 18° C., is most to be recommended.

5. The method must admit of the substance being rubbed fine, for in no other way can uniformity in the results be obtained.

6. A sufficient quantity of the menstruum must be available for rubbing up the substance. 100 cc. of citrate solution are not enough for conveniently dealing with 5 grams of substance.

7. The determination of the phosphoric acid must be made in the extract and not indirectly in the residue, and the phosphoric acid must be precipitated by molybdenum, so that the results turn out exact and reliable.

Having regard to these seven essentials, I arrived, after many experiments, at the following method: 5 grams of superphosphate or precipitated phosphate are rubbed up with some dilute citrate solution, poured into a half-litre flask, made up to the mark with dilute citrate solution, allowed to stand about 18 hours at the temperature of the room (13° to 18° C.), with frequent shaking, and then filtered.

50 cc. of the filtrate are then treated with molybdenum solution, so that 1 cc. shall be present for every milligram of phosphoric acid, and to this mixture as much concentrated ammonium nitrate solution is added as would amount to a fourth of the mixture. After standing for about twenty minutes in the water-bath it is allowed to cool and is then filtered; the precipitate is washed on to the filter with a dilute solution of ammonium nitrate, a hole made in the filter, and the precipitate washed back into the beaker with dilute ammonia (2½ per cent.); the filter is well washed, and to the ammoniacal solution 20 cc. of magnesia mixture are added drop by drop with constant stirring. After standing for one hour the precipitate is filtered off, washed with dilute ammonia (2 per cent.), dried and ignited.

Preparation of the Necessary Solutions.

1. Concentrated citrate solution. 150 grams of citric acid are placed in a litre flask, dissolved in water, and neutralised with ammonia. To the neutralised solution 10 grams of citric acid are added, and the solution made up to the mark with water.

2. Dilute citrate solution. 1 volume of concentrated citrate solution is mixed with 4 volumes of water.

3. Concentrated ammonium nitrate solution. 750 grams of ammonium nitrate are dissolved in water and the solution diluted to a litre.

4. Dilute ammonium nitrate solution. 100 grams of ammonium nitrate are dissolved in water and the solution diluted to a litre.

5. Molybdenum solution. 150 grams of ammonium molybdate are dissolved in water, the solution diluted to a litre, and mixed with a litre of nitric acid of sp. gr. 1.2.

6. Magnesia mixture. 110 grams of pure crystallised magnesium chloride and 140 grams of ammonium chloride are dissolved in 1300 cc. of water and 700 cc. of ammonia (8 per cent.).

I now give the results I obtained by this method in comparison with those calculated from the mean results of the manurial experiments.

"Soluble" Phosphoric Acid.

	Calculated from the results of the manurial experiments. Per cent.	Obtained by analysis. Per cent.
Bicalcium phosphate, ...	30.6	29.3
Tricalcium "	18.0	19.1
Washed-out high-class superphosphate, .	17.9	16.9
" phosphorite " .	3.0	3.3
Finely ground phosphorite, . . .	0.1	0.6

These results agree satisfactorily, and it may be reasonably accepted that my method gives figures which show sufficiently near the truth the agricultural value of phosphorite superphosphate, high-class superphosphate, and precipitated phosphate in terms of phosphoric acid soluble in water.

It is now self-evident that the method could be further developed, and had not external pressure been brought to bear upon me, I would have hesitated before proposing to introduce it at once into the practice of the manure trade. Requests to make determinations of phosphoric acid soluble in citrate in the above-named manure materials have, however, been so frequent of late at the experimental stations at Bonn, Darmstadt, Speier and Wiesbaden that the immediate introduction of the method appeared very necessary.

At a meeting of those manure manufacturers of South Germany chiefly interested, held at Mayence on November 30th, 1885, and called at the instance of the experimental stations of Bonn, Darmstadt, Marburg, Speier and Wiesbaden, I found myself called upon to report upon the work I had carried out, and to apply to them to test my process as to what extent in the various laboratories concordant results could be obtained. In consequence of this request

the meeting appointed representatives of four experimental stations and four manure works as a commission, which carefully drew average samples of 8 different phosphatic manures and distributed them amongst 12 laboratories, and at a further meeting held at Mayence, on December 19th, reported upon the results obtained.

From the returns furnished by 11 of the laboratories it was ascertained that the variations between the separate results and the mean averaged as follows:

	Per cent. "soluble" phosphoric acid.
With high-class superphosphate, . .	I = ±0.27
" " " . .	II = 0.38
With phosphorite " . .	III = 0.30
" " " . .	IV = 0.32
	Mean = ±0.32

Against this the variations in the determinations of the phosphoric acid soluble in water made by the same chemists amounted to—

	Per cent. phosphoric acid soluble in water.
With high-class superphosphate, . .	I = ±0.39
" " " . .	II = 0 36
With phosphorite " . .	III = 0.13
" " " . .	IV = 0.18
	Mean = ±0.26

From this we see that the mean differences in the determinations of the "soluble" phosphoric acid exceed those of the phosphoric acid soluble in water by only 0.6 per cent. The representatives of the manure manufacturers and those of the experimental stations of Bonn, Darmstadt, Speier and Wiesbaden have therefore agreed unanimously to accept this method for the analysis of all superphosphates from January, 1886, and in consequence thereof, to advertise in their price lists a guaranteed percentage of "soluble" phosphoric acid in the different superphosphates.

In the case of Thomas precipitated phosphate the results obtained were not sufficiently concordant, and the commission was requested to look closer into the matter and to report again in due course.

It is now to be hoped that the convention which met at Mayence, as well as all other manure manufacturers and agricultural chemists, will co-operate in this movement, in order that through the instrumentality of this agreement this most desirable reform in the trade in precipitated or "reverted" phosphates may be carried out in the interests of buyers and sellers alike.

PAUL WAGNER.

STUDIES FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, SHEFFIELD SCIENTIFIC SCHOOL OF YALE COLLEGE, 1884–85. Edited by R. H. CHITTENDEN, Ph. D. New Haven: Tuttle, Morehouse & Taylor. 1885.

The appearance of this volume of 200 pages, in addition to the numerous articles from this laboratory that have been published in the journals, is a pleasant surprise to those interested in physiological chemistry. The "Studies" consist of eleven papers contributed by Prof. Chittenden and his co-workers. The first seven of these are devoted to a record of investigations on the soluble ferments, with special reference to the action of various agents on these bodies. These experiments are of unusual interest at the present time, when so much attention is being given to similar observations on the organised ferments. The similarity that is shown to exist between the action of most agents on the two classes of ferments suggests the question as to how far the antiseptic value of an agent is dependent on its action on the soluble ferments secreted by the organism. It is to be hoped that work of this character will place our knowledge of antiseptics on something more than the present empirical basis. The disputed point concerning the amount of acid necessary to prevent the action of diastase is taken up by the authors, and they show that it depends simply upon the amount of proteid matter in the solution, the acid combining with this to form acid-proteids, which act very differently from free acid.

A short paper on "Absorption of Arsenic by the Brain" gives two new cases in support of the editor's view, "that the amount of arsenic present in the brain, in cases of arsenical poisoning, is an index to the form in which the poison was taken."[1]

Two papers on the "Influence of Potassium and Ammonium Bromides," and of "Cinchonidine Sulphate on Metabolism," are of considerable physiological interest.

The concluding paper is devoted to a review of the work of Seegen and others on the "Post-mortem Formation of Sugar in the Liver in the Presence of Peptones," and contains also a large number of additional experiments on this subject. The conclusions reached by the authors appear to be decisive, from the fact that they have overcome the principal difficulty of former investigators —viz.: that of making accurate determinations of the various hydrocarbons in the presence of albuminoid matter.

The volume owes its interest both to the importance of the subjects investigated, and to the large amount of careful work from which the results have been obtained. The introduction of accurate chemical analyses into physiological research seldom fails to be of use to both sciences. J. R. D.

[1] This Journal **5**, 8.

NOTES.

Editor AMERICAN CHEMICAL JOURNAL.

SIR:—As a large number of persons employ Laurent's polariscope for the estimation of sugar, I desire to call their attention, through your Journal, to a peculiarity in the method of graduation which has the effect of making all the results obtained with the instrument too low. I had prepared a paper explaining the matter at length, as it had gradually made itself known to me, but to-day see in the *Bulletin de l'Association des Chemistes* **3,** 255–259, an article by D. Sidersky correcting the same error. I therefore merely wish to bring the main points before your readers, referring them to the original paper of Sidersky for greater details.

The Laurent instrument is graduated with a plate of quartz and not with a definite solution of pure sugar. The plate of quartz is exactly one millimeter thick, and it is accepted by Laurent from the researches of Girard and De Luynes that this has an angular rotation of 24°40′ corresponding to a sugar solution containing 16.19 grams per 100 cc. Recent researches of Tollens and Schmitz have independently shown that the $[a]_D$ for a concentration of about ten per cent. is 66.5°, and this is without doubt the most reliable figure we have to-day to go by. Comparing Laurent's graduation with this, we see that the normal weight for his instruments is somewhat at fault. From his data he makes 100° of the sugar scale correspond to 24°40′ of the angular. Combining these figures with the specific rotatory power given by Tollens for solutions of about normal strength in the well-known formula,

$$[a]_D = \frac{100a}{lC},$$

we get from our data, where the usual 200 mm. tube is used,

$$66.5° = \frac{100 \times 24.6666}{200 \times C} \quad \text{or} \quad C = \frac{246 \times 6.66}{133.0}.$$

The construction or normal weight calculated from this equation is 16.29, or a tenth of a gram more than Laurent gives as the correct one for his instrument; but it is undoubtedly the correct one to use, as has been proved by Sidersky, and by experiments in the Laboratory of the Department of Agriculture.

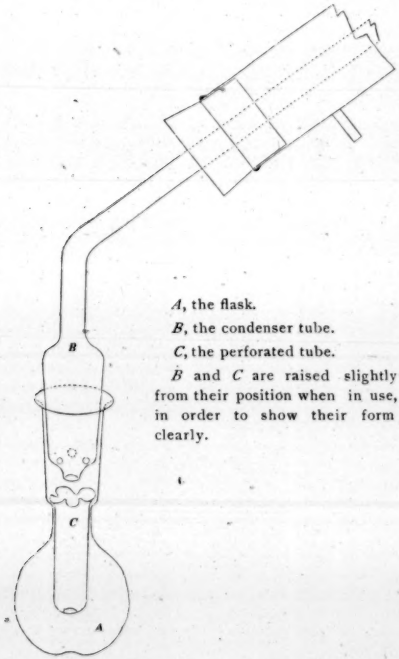
Trusting that this note may prove of interest to some of your readers, and save them from some annoyingly low results in polarising high-grade refined sugars, I am

Very truly yours,

CLIFFORD RICHARDSON.

On a New Apparatus for the Continuous Extraction of Solids by a Volatile Solvent.[1]

The authors have devised a new form of extraction apparatus which is so satisfactory to them that they think that a brief description of it may be of interest to other chemists. It consists of three parts: the flask *A*, the condenser *B*, and the perforated



A, the flask.
B, the condenser tube.
C, the perforated tube.
B and *C* are raised slightly from their position when in use, in order to show their form clearly.

tube *C*. The flask is 14–15 cm. in height, and weighs about 45 grams. The upper part of the neck is ground to fit the condenser, and is 3 cm. in diameter. The lower part of the neck contracts suddenly to 2.5 cm. in diameter, thus presenting an annular projection within which supports the perforated tube. The tube of

[1] This apparatus was described before the Kansas Academy of Science, Nov. 11, 1885.

the condenser is about 75 cm. long, and has an internal diameter of 8 mm. Near the lower end it is bent at an angle of 60°, and passes upward through a copper tube 3–4 cm. in diameter, supplied with cold water when in use. At its lower end the condenser tube expands into a stopper for the flask, and at its extremity is brought nearly to a point, to direct the dropping of the condensed solvent. Three additional openings are made in the stopper-expansion to allow the vapor free passage upward. The perforated tube is similar to a short, wide test tube, with a perforation in the bottom. The lip of the tube is notched to give openings for the passage of the vapor. The body of the tube must pass readily through the contraction in the neck of the flask, and at the same time the lip must rest securely on the inner projection. The lower end of the tube may reach within 1.5–2 cm. of the bottom of the flask.

The mode of using the apparatus is almost obvious. The substance to be treated is confined in the perforated tube between two layers of asbestus, a sufficient amount of the volatile solvent is placed in the previously weighed flask, and the parts are put in place and suitably supported. Upon heating the solvent by means of a water-bath, the vapor is evolved with any rapidity desired, and passes into the condenser. The condensed solvent flows uninterruptedly down the same tube, drops into the perforated tube, filters through the substance to be extracted, and passes back into the flask. After the operation has been continued as long as is desired the perforated tube is removed, the apparatus inclined so as to carry the condensation out instead of back, and the solvent distilled off. The solvent may thus be recovered, which is a matter of no small importance where ether is used and many determinations are to be made. The flask, with the substance extracted, is then carefully dried and weighed.

The chief advantages of this extractor are its simplicity, and consequent convenience of handling, and its freedom from corks which come in contact with the solvent. It avoids the slender tubes and multiplicity of connections so common in extractors, and at the same time can be manufactured at a very moderate cost. Every chemist knows the difficulty and inconvenience of completely removing the soluble substances from corks, but if it is desired the flask can be made without having the neck ground, and it can be connected by a cork to an inverted Liebig's condenser. In this form the extractor is still cheaper, and, even with the one cork, is more desirable than any other form that has come under our notice.

This apparatus was designed for quantitative work, but, with some modifications, might be adapted to pharmaceutical operations. The flask would have to be made deeper and the neck much wider, so as to admit a large perforated tube. The flask could be connected with the condenser by means of a broad ring of glass, ground on its outer edge to fit the neck of the flask and within to fit the condenser tube. In that way an apparatus could

be constructed of considerable capacity, and, we think, at less cost than those now in use.

G. H. FAILYER AND J. T. WILLARD.
KANSAS STATE AGRICULTURAL COLLEGE.

The Action of Nitric Acid on Mercuric Sulphide.

Probably many chemists have had their attention called to the difficulty in the qualitative determination of mercury mentioned in Prof. Torrey's note in the JOURNAL for December, '85. Following Fresenius, most manuals of qualitative analysis state that the mercury is found as a black, insoluble residue after the mixed sulphides are treated with nitric acid. The manual of Dr. F. P. Venable (Univ. of N. C.) is the only one in my knowledge which mentions that "the residue may be HgS (black), (HgS)$_2$ $Hg(NO_3)_2$ (*white*)," etc.

Most authorities state that HgS is unaffected by dilute nitric acid. Watts says (Vol. III, p. 913), "It (HgS) withstands the action of most solvents, but is decomposed with separation of sulphur by very strong nitric acid; dilute nitric acid *has scarcely any action upon it*" (italics mine); which in the first supplement is modified to "mercuric sulphide, which under ordinary circumstances is insoluble in nitric acid, is likewise converted, by prolonged heating with that acid, into the white compound $Hg(NO_3)_2$ 2HgS" (Vol. VI, p. 818).

In my own experience I have been unable to effect any change in mercuric sulphide by boiling with pure nitric acid (sp. gr. 1.42), but on the addition of a single drop of dilute hydrochloric acid (1 : 3) to the boiling nitric acid, the sulphide was immediately converted into a yellowish-white compound, presumably the $Hg(NO_3)_2$ 2HgS. On the addition of a very small further quantity (say ten drops) of the dilute hydrochloric acid, this white compound dissolved easily and completely. The sulphide was also easily acted on by boiling dilute nitric acid when a very small quantity of hydrochloric acid was present, and dissolved to some extent.

Now, since most nitric acid, except reliable c. p. acid, contains traces of hydrochloric acid, it will be easily understood how these differences of opinion have originated, and that the mercury must not be overlooked in the white residue, after treating the mixed sulphides with dilute nitric acid.

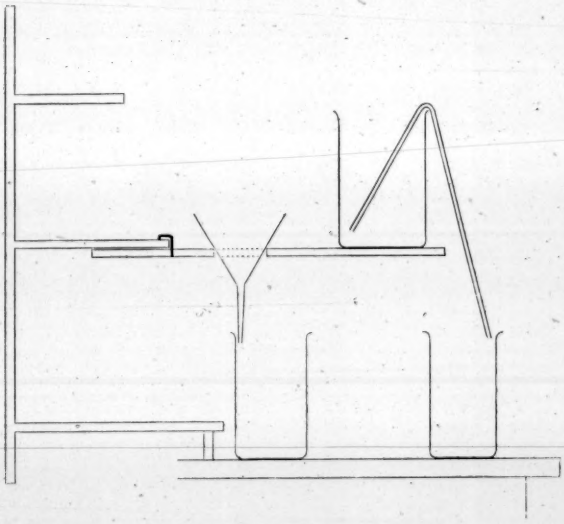
I have often known traces of mercuric sulphide to be thus dissolved, and, since the precipitate of mercuric nitrate with ammonia, like that of cadmium and copper, is easily soluble in excess of ammonia, and in this solution is not precipitated by potassium cyanide, to be precipitated by hydrogen sulphide in the test for cadmium.

The moral of this is to use only a nitric acid which is known to be pure for the solution of the mixed sulphides.

JAS. LEWIS HOWE.
LABORATORY OF CENTRAL UNIVERSITY, RICHMOND, KY., *January*, 1886.

A New Funnel Support.

The following simple device will often be found of use on the working desk in the laboratory, where space must be economised. It consists of a piece of dressed inch plank about 20 by 8 inches; at a distance of 5 or 6 inches from one end two stout wrought-iron hooks are driven and clinched. The working desk must be provided with firmly fixed shelves, such as are usually employed for reagents. The end of the plank is pushed under a shelf and is held in place by the hooks, which catch upon the edge of the shelf. The portion of the plank projecting over the desk may then be employed as a support for funnels, percolators, etc. The figure presents in part a cross-section of a desk with the support in use.



A support of this description, in which six or more holes of different sizes are cut, will often replace several filter stands, tripods, etc., which require so much more space for their accommodation, both when they are in use and when out of use.

F. P. DUNNINGTON.

UNIVERSITY OF VIRGINIA, *January*, 1886.